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A methodology is presented for estimating the multimedia environmental loadings for a "new" chemical, in the absence of manufacturing plant emission data. The methodology draws on an environmental release data base that contains multimedia environmental loadings for structurally similar compounds that undergo similar process (physical and chemical) unit operations. The data base is integrated with other pertinent avaliable data on the manufacturing process of the new chemical such as (1) physical and chemical properties of process feedstock, products and byproducts; (2) reaction stoichiometry, thermodynamics and reaction kinetics; (3) process flow diagram and process mass balance; (4) location and composition of environmental releases and method of disposal; (5) process environmental control technology including performance; (6) process storage and handling requirements; and (7) plant equipment components (in numbers and classes). In practice, sufficient direct data are rarely avaliable for estimating the environmental loadings of the compound under review; the methodology has been designed with this reality in mind. In every case, where data deficiencies are likely to occur, alternative means are suggested for filling the data gaps. The methodology integrates all pertinent data to enable the user to estimate multimedia (controlled and uncontrolled) environmental loadings under the classifications of storage and handling, process and fugitive emissions, respectively. An example is provided to demonstrate the methodology's applicability.

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METHODOLOGY FOR ESTIMATING ENVIRONMENTAL LOADINGS FROM MANUFACTURE OF SYNTHETIC ORGANIC CHEMICALS

by

Donal T. O'Leary
Kathleen M. Richter
Pamela A. Hillis
Patricia H. Wood
Sarah E. Campbell

Versar Inc.
6621 Electronic Drive
Springfield, Virginia 22151

Contract No. 68-03-3061

Project Officer
Kenneth F. Hedden
Technology Development and Applications Branch
Environmental Research Laboratory
Athens, Georgia 30613

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL RESEARCH LABORATORY
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FOREWORD

Environmental protection efforts are increasingly directed towards prevention of adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops appropriate transport and transformation measurement protocols, source information, and environmental data bases for application to models that assess toxic chemical exposure.

Delineation of the environmental pathways followed by potentially harmful chemicals is a key element in predicting the effects of pollutants before extensive damage occurs. This report presents a methodology for obtaining source identification and environmental loading information for use in evaluating some of the important pathways of chemicals in aquatic and atmospheric environments.

William T. Donaldson
Acting Director
Environmental Research Laboratory
Athens, Georgia

ABSTRACT

A methodology is presented for estimating the multimedia environmental loadings for a "new" chemical, in the absence of manufacturing plant emission data. The methodology draws on an environmental release data base that contains unit processes multimedia environmental loadings for structurally similar compounds that undergo similar process (physical and chemical) unit operations. The data base is integrated with other pertinent available data on the manufacturing process of the new chemical such as (1) physical and chemical properties of process feedstock, products and byproducts; (2) reaction stoichiometry, thermodynamics and reaction kinetics; (3) process flow diagram and process mass balance; (4) location and composition of environmental releases and method of disposal; (5) process environmental control technology (including performance); (6) process storage and handling requirements; and (7) plant equipment components (in numbers and classes).

In practice, sufficient direct data are rarely available for estimating the environmental loadings of the compound under review; the methodology has been designed with this reality in mind. In every case, where data deficiencies are likely to occur, alternative means are suggested for filling the data gaps. The methodology integrates all pertinent data to enable the user to estimate multimedia (controlled and uncontrolled) environmental loadings under the classifications of storage and handling, process, and fugitive emissions, respectively. An example is provided to demonstrate the applicability of the methodology.

This report was submitted in partial fulfillment of Contract No. 68-03-3061 to Versar, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1981, to April 1982, and work was completed as of January 1983.

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency is charged with the responsibility for identifying, evaluating, and regulating a variety of chemical and radiological hazards to human health and the environment under the authorities of statutes such as the Toxic Substances Control Act (TSCA), the Clean Air Act (CAA), the Clean Water Act (CWA), the Safe Drinking Water Act (SDWA), the Federal Insecticide, Fungicide, and Rodentcide Act (FIFRA), and the Atomic Energy Act (AEA). For understanding and quantifying the nature and magnitude of the hazards presented by chemical and radiological agents and for isolating the most suitable (regulatory and technological) control options, exposure assessments form an essential part of the regulatory decision making process.

Section 5 of the Toxic Substances Control Act (TSCA), requires the EPA to consider "the extent to which a use [of the chemical] changes the type or form and/or increases the magnitude and duration of exposure of human beings or the environment." The conduct of an exposure assessment necessitates the provision and utilization of reliable environmental release data, especially for new organic chemicals. These chemicals are frequently referred to as pre-manufacturing notice (PMN) chemicals because of the requirement that industry must inform the EPA of their plan to manufacture the compound enables the EPA to meet its regulatory responsibilities.

This report presents a methodology for estimating multimedia environmental loadings of a "new" organic chemical (Section 2), the output data of which can be used to determine population exposure (within and without the manufacturing process plant battery limits) and to isolate the most suitable control options. Section 3 illustrates how the methodology is used to determine the multi-media environmental loadings associated with the manufacture of a "typical" chemical. Finally, Section 4 presents the conclusions drawn from the study.

1.1 PRELIMINARY REMARKS ON THE METHODOLOGY

The determination of the battery limits environmental loadings associated with the production of a "new" compound of the Synthetic Organic Chemical Manufacturing Industry (SOCMI) is aided by classifying the environmental loadings under the major headings, storage and handling emissions, process releases, and fugitive emissions. Storage and handling emissions occur during the storage and handling of plant items such as feedstock, intermediates, final products, usable by-products, waste tars, residues, non-usable by-products plus their tankage on site. Process releases are caused by the manufacturing process itself and can be related (both qualitatively and quantitatively) to each major unit operation in the manufacturing process train. Fugitive emissions are defined as those emissions that result from leaking plant equipment components such as pump-seals, in-line (process and control) valves, relief valves, open-ended (sample, drain, vent) valves, compressor seals, flanges, and cooling towers.

For a precise determination of the environmental loadings associated with the production of a "new" SOCMI compound, it is necessary to conduct a rigorous field monitoring survey. Insofar as PMN chemicals are concerned, this situation rarely if ever occurs primarily because the chemical heretofore may never have been manufactured commercially. In the absence of plant data, a confident estimate of plant emissions can be made by integrating the following data:

- The manufacturing practices' and unit processes' multimedia environmental loadings for structurally similar compounds that undergo analogous process (physical and chemical) unit operations trains.
- Physical and chemical properties of process feedstock, products, and by-products.
- Reaction stoichiometry, thermodynamics, and reaction kinetics.
- Process flow-diagram and process mass-balance.
- Location/composition of environmental releases and method of disposal.

- Process environmental control technology (including performance).
- Process storage and handling requirements.
- Plant equipment components (in numbers and classes).

In practice, available direct data on the compound under review are usually limited, and the methodology has been designed with this reality in mind (see Figure 1). In every case, where data deficiencies are likely to occur, alternative means are suggested for filling the data gaps. The methodology integrates all pertinent data to enable the user to estimate multimedia (controlled and uncontrolled) environmental loadings under the classifications of process, storage and handling, and fugitive releases, respectively.

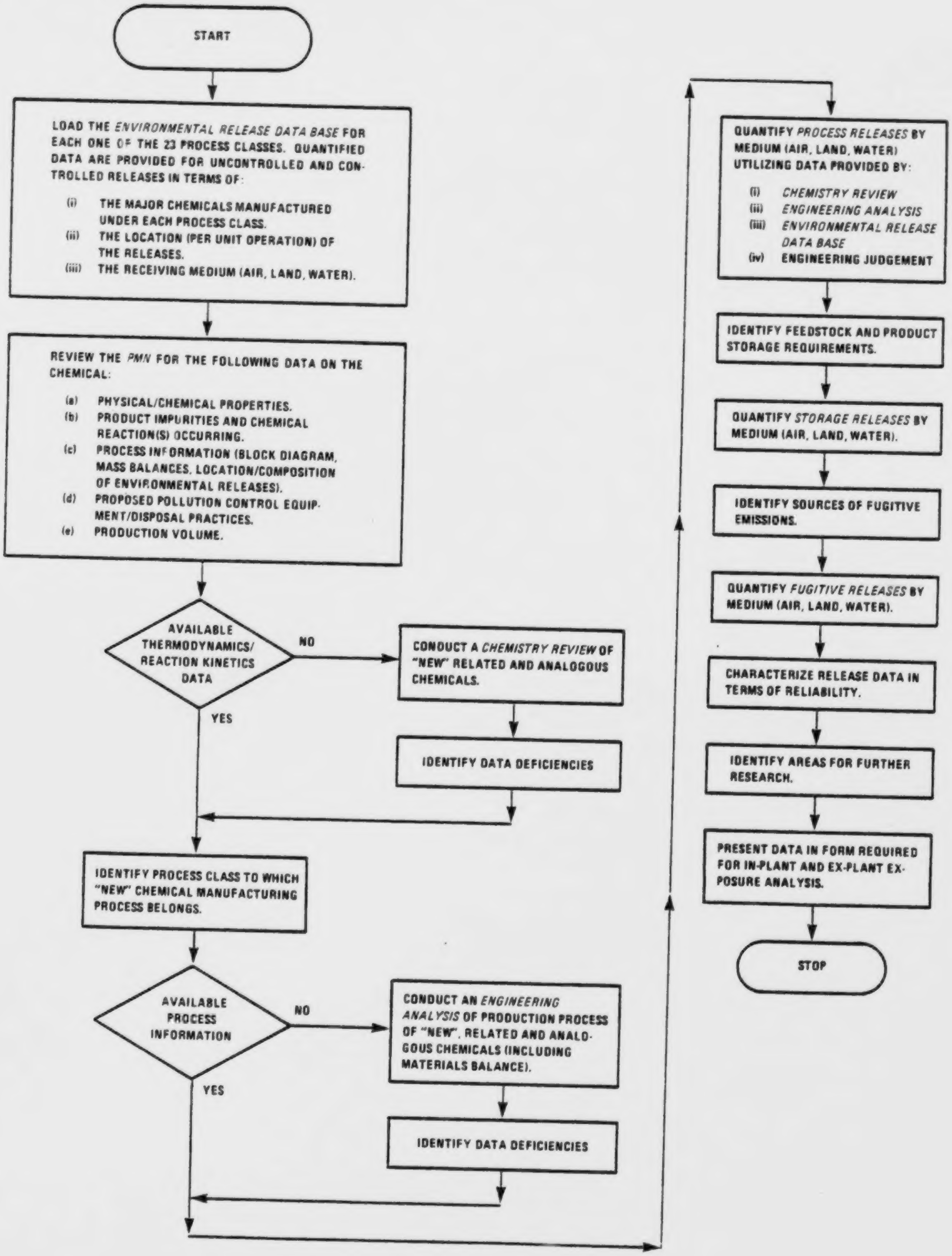
START
LOAD THE ENVIRONMENTAL RELEASE DATA BASE FOR EACH ONE OF THE 23 PROCESS CLASSES. QUANTIFIED DATA ARE PROVIDED FOR UNCONTROLLED AND CONTROLLED RELEASES IN TERMS OF:
(i) THE MAJOR CHEMICALS MANUFACTURED UNDER EACH PROCESS CLASS.
(ii) THE LOCATION (PER UNIT OPERATION) OF THE RELEASES.
(iii) THE RECEIVING MEDIUM (AIR, LAND, WATER).
REVIEW THE PMN FOR THE FOLLOWING DATA ON THE CHEMICAL:
(a) PHYSICAL/CHEMICAL PROPERTIES.
(b) PRODUCT IMPURITIES AND CHEMICAL REACTION(S) OCCURRING.
(c) PROCESS INFORMATION (BLOCK DIAGRAM, MASS BALANCES, LOCATION/COMPOSITION OF ENVIRONMENTAL RELEASES).
(d) PROPOSED POLLUTION CONTROL EQUIPMENT/DISPOSAL PRACTICES.
(e) PRODUCTION VOLUME.
AVAILABLE THERMODYNAMICS/ REACTION KINETICS DATA
NO
CONDUCT A CHEMISTRY REVIEW OF "NEW" RELATED AND ANALOGOUS CHEMICALS.
IDENTIFY DATA DEFICIENCIES
YES
IDENTIFY PROCESS CLASS TO WHICH "NEW" CHEMICAL MANUFACTURING PROCESS BELONGS.
AVAILABLE PROCESS INFORMATION
NO
CONDUCT AN ENGINEERING ANALYSIS OF PRODUCTION PROCESS OF "NEW", RELATED AND ANALOGOUS CHEMICALS (INCLUDING MATERIALS BALANCE).
IDENTIFY DATA DEFICIENCIES
YES
QUANTIFY PROCESS RELEASES BY MEDIUM (AIR, LAND, WATER) UTILIZING DATA PROVIDED BY:
(i) CHEMISTRY REVIEW
(ii) ENGINEERING ANALYSIS
(iii) ENVIRONMENTAL RELEASE DATA BASE
(iv) ENGINEERING JUDGEMENT
IDENTIFY FEEDSTOCK AND PRODUCT STORAGE REQUIREMENTS.
QUANTIFY STORAGE RELEASES BY MEDIUM (AIR, LAND, WATER).
IDENTIFY SOURCES OF FUGITIVE EMISSIONS.
QUANTIFY FUGITIVE RELEASES BY MEDIUM (AIR, LAND, WATER).
CHARACTERIZE RELEASE DATA IN TERMS OF RELIABILITY.
IDENTIFY AREAS FOR FURTHER RESEARCH.
PRESENT DATA IN FORM REQUIRED FOR IN-PLANT AND EX-PLANT EXPOSURE ANALYSIS.
STOP

FIGURE 1. PROCEDURE FOR THE DETERMINATION OF THE ENVIRONMENTAL LOADING OF A "NEW" CHEMICAL

2.0 THE METHODOLOGY

The methodology may be understood in terms of ten steps:

1. Load the environmental release data base.
2. Review the PMN.
3. Conduct a chemistry review.
4. Conduct an engineering analysis.
5. Identify and quantify process releases.
6. Identify and quantify storage and handling emissions.
7. Identify and quantify fugitive emissions.
8. Characterize release data in terms of reliability.
9. Identify areas for further research.
10. Present data in form required for in-plant and ex-plant exposure analyses.

The actions that need to be taken under each of the ten steps are detailed below.

2.1 LOADING of THE ENVIRONMENTAL RELEASE DATA BASE (ERDB)

The first step in estimating the environmental release of a "new" chemical is the loading of the environmental release data base. This data base brings together available emissions data for the 23 major unit processes of the synthetic organic chemicals manufacturing industry (SOCMI). It will be described in terms of its organization and data sources.

2.1.1 Organization of the ERDB

The ERDB is organized into 23 categories that correspond to the 23 major large-volume SOCMI "unit process" components that carry out the fundamental synthesis reactions e.g., alkylation, halogenation. Conceptually, the unit process is useful in that for a given unit process, the physical or organic chemistry of the compounds within that unit process tends to be alike or similar. The significance of the process waste streams and the industrial importance of the compounds produced were also considered in the selection of the major unit processes. A listing of the

23 major unit processes and the total number of compounds produced commercially using these processes is given in Table 1 [Herrick et al. 1979].

For each unit process, available release data have been compiled for the large-volume SOCMI chemicals manufactured by the named unit process. Environmentally controlled and uncontrolled release data are presented for the three classes (process, storage and handling, and fugitive) in terms of the receiving medium (air, land, water). Process releases are further classified in terms of the unit operations that occasion the emissions. Table 2 is a listing of chemical products for which manufacturing process multimedia emissions data are provided in the environmental release data base. For each medium, the data source is identified plus an indication of whether quantified or unquantified data are available.

The Environmental Release Data Base (ERDB) [enclosed as Appendix A] is extracted from reports that were prepared on the principal unit processes. The format for each report is shown in Appendix B.

2.1.2 Data Sources Used in Preparing the ERDB

The data sources that were used to prepare the ERDB are listed in Table 1-2 of Appendix A. They are classified according to year of publication, basis used for reporting emissions data (plant sampling, materials balance, estimated data), explicitness of reported emissions data to plant production levels, form of reported emissions, vintage of reported data, level of data uncertainty (ranging from Level 1 (the best) -- emissions estimated from company site visit data -- to level 4 (the worst) -- emissions of indeterminate accuracy estimated without supporting data).

All except two of the reports are based on studies that were conducted by the Environmental Protection Agency or its contractors.

TABLE 1. 23 MAJOR UNIT PROCESSES-SUMMARY

Process	Compounds
1. Alkylation	15
2. Amination by Ammonolysis	13
3. Ammoxidation	10
4. Carbonylation (oxo)	10
5. Condensation	55
6. Cracking (catalytic)	3
7. Dehydration	6
8. Dehydrogenation	15
9. Dehydrohalogenation	6
10. Esterification	24
11. Halogenation	54
12. Hydrodealkylation	3
13. Hydrogenation	27
14. Hydrohalogenation	7
15. Hydrolysis (hydration)	28
16. Nitration	12
17. Oxidation	47
18. Oxyhalogenation	5
19. Phosgenation	3
20. Polymerization	34
21. Pyrolysis	20
22. Reforming (steam)-Water Gas Reaction	1
23. Sulfonation	11
TOTAL	410

Table 2 Product Index of Unit Processes and Feedstocks for Manufacture of 263 Commercial Organic Chemicals

Product	Other Products	Processes	Feedstock
1. Acetaldehyde	None	Dehydrogenation	Ethyl alcohol
Acetaldehyde	None	Oxidation	Ethylene
2. Acetic Acid	None	Alkylation Oxidation	n-Butenes
Acetic Acid	None	Oxidation	Light naphtha
Acetic Acid	Peracetic acid	Oxidation	Acetaldehyde
Acetic Acid	Terphthalic acid	Oxidation	n-Butane, p-xylene
Acetic Acid	Methanol	Hydrolysis	Methyl acetate
Acetic Acid	None	Carbonylation (oxo)	Methanol, Carbon monoxide
3. Acetic Anhydride	None	Condensation Pyrolysis	Acetic acid
4. Acetone	None	Dehydrogenation	Isopropyl alcohol
Acetone	Phenol	Acid cleavage, Alkylation	Benzene, Propylene
Acetone	Phenol	Hydrolysis, Oxidation Acid cleavage, Oxidation	Cumene
5. Acetylene	Ethylene	Oxidation Cracking (atalytic)	Hydrocarbons (C_1-C_8)
Acetylene	None	Pyrolysis by electric arc	Hydrocarbons (C_1-C_8)
6. Acrolein	Acetaldehyde Acrylic acid	Oxidation	Propylene
7. Acrylamide	None	Hydrolysis	Acrylonitrile
8. Acrylic Acid and Acrylate Esters	None	Esterification Oxidation	Propylene, Alcohols
9. Acrylic Resins	None	Polymerization	Acrylonitrile
10. Acrylonitrile	None	Ammoxidation	Propylene
Acrylonitrile	None	Hydrocyanation	Acetylene Hydrogen cyanide

Table 2, continued

Product	Other Products	Processes	Feedstock
11. Acrylonitrile-Butadiene Styrene Resins (ABS resins)	None	Polymerization	Acrylonitrile, Butadiene, Styrene
12. Adipic Acid	None	Oxidation	Cyclohexane
Adipic Acid	None	Oxidation	Cyclohexyl alcohol
13. Adiponitrile	None	Ammoxidation	Adipic acid
Adiponitrile	Hexamethylene diamine	Halogenation Hydrogenation	Butadiene
Adiponitrile	None	Electrohydrodimerization	Acrylonitrile
14. Alcohols (C_7-C_{13})	None	Carbonylation (oxo)	Methanol, Carbon monoxide
15. Alcohols, Mixed, Linear Sulfated, Ammonium Salt	None	Sulfonation	Fatty alcohols, SO_3
-, Sodium Salt	None	Sulfonation	Fatty alcohols, SO_3
-, Triethanomine Salt	None	Sulfonation	Fatty alcohols, SO_3
-, Unspecidied	None	Sulfonation	Fatty alcohols, SO_3
16. Alkyl Benzenes (branched)	None	Alkylation	Benzene Propylene tetramer
Alkyl Benzenes (linear)	None	Alkylation	Benzene, linear olefins
Alkyl Benzenes (linear)	None	Alkylation Dehydrogenation	Benzene, linear parafins
17. Alkylbenzene Sulfonates	None	Hydrolysis Sulfonation	Alkyl benzenes, Sulfur tioxide

Table 2, continued

	Product	Other Products	Processes	Feedstock
18.	Allyl Chloride	None	Halogenation	Propylene
19.	m-Aminophenol	None	Hydrogenation Hydrolysis Sulfonation	Nitrobenzene
20.	o-Aminophenol	None	Amination by reduction Nitration	Phenol
21.	p-Aminophenol	None	Acid Rearrangement Hydrogenation	Nitrobenzene
22.	Aniline	None	Hydrogenation	Nitrobenzene
	Aniline	None	Ammination by ammonolysis	Phenol
23.	Anthraquinone	None	Oxidation	Anthracene
24.	Arsanilic Acid	None	Condensation	Aniline, Arsenic acid
25.	Azeliac Acid	Caproic acid Pelargonic acid	Ozonolysis Oxidation	Oils (tall, red, soya bean)
26.	Benzene	Xylenes	Alkylation	Tluene
	Benzene	None	Hydrodealkylation	Coke oven light oil
	Benzene	None	Hydrodealkylation	Toluene
	Benzene	None	Hydrodealkylation	Xylenes (mixed)
	Benzene	Light hydrocarbons	Hydrodealkylation	Aromatic mixtures
27.	Benzenesulfonamide	None	Amination by ammonolysis	Benzenesulfonyl chloride
28.	Benzenesulfonyl Chloride	None	Condensation	Benzene, Chlorosulfonic acid
29.	Benzoic Acid	None	Oxidation	Toluene
30.	Benzonitrile	None	Ammoxidation	Toluene
31.	Benzyl Chloride	None	Halogenation	Toluene
32.	Biphenyl	None	Condensation	Benzene

Table 2, continued

	Product	Other Products	Processes	Feedstock
33.	Bisphenol A	None	Condensation	Acetone, Phenol
34.	1,3-*bis*(aminomethyl)cyclohexane	None	Hydrogenation	Isophthalonitrile
35.	Bromoform	None	Halogenation	Acetone, Bromine
36.	Butadiene	None	Dehydrogenation (catalytic)	*n*-Butane
	Butadiene	None	Dehydrogenation (catalytic)	Butene-1, Butene-2
	Butadiene	None	Dehydrogenation (oxidative)	Butene-1, Butene-2
37.	*n*-Butyl Acetate	None	Esterification	Acetic acid, *n*-Butyl alcohol
38.	*n*-Butyl Acrylate	None	Pyrolysis	Acetic acid, *n*-Butyl alcohol
39.	*n*-Butyl Alcohol	*n*-Butyraldehyde	Carbonylation (oxo) Hydrogenation	Propylene, Carbon
	n-Butyl Alcohol	Crotonaldehyde *n*-Butyraldehyde	Condensation Hydrogenation	Acetaldehyde
40.	*sec*-Butyl Alcohol	None	Hydrolysis	Butylene
	sec-Butyl	None	Sulfonation Hydrolysis	Butene-1, Butene-2
41.	*tert*-Butyl Alcohol	None	Oxidation	Isobutane
42.	*n*-Butyl Benzel Phthalate	None	Esterification	Benzyl alcohol, *n*-alcohol Phthalic anhydride
43.	*p*-*tert*-Butyl Phenol	None	Alkylation	Isobutene, Phenol
44.	*n*-Butyraldehyde	*n*-Butyl alcohol Crotonaldehyde	Condensation Hydrogenation	Acetaldehyde
	n-Butyraldehyde	*n*-Butyl alcohol		Propylene, Carbon monoxide

Table 2, continued

	Product	Other Products	Processes	Feedstock
45.	Caproic Acid	Azeliac acid	Oxidation	Oils (tall, red, soya bean)
46.	Caprolactam	None	Acid rearrangement Hydrogenation Oxidation	Toluene, Ammonia
	Caprolactam	None	Beckmann rearrangement Oxidation Oximation	Cyclohexane, Ammonia Oleum
	Caprolactam	None	Beckmann rearrangement Oximation	Ammonia, Oleum Cyclohexanol, Cyclohexanone
47.	Carbon Tetrachloride	None	Halogenation	Carbon disulfide
	Carbon Tetrachloride	Perchloroethylene	Halogenation	Methane, Propane
	Carbon Tetrachloride	Perchloroethylene	Halogenation	Propane/Propylene
48.	Choline Chloride	None	Amination by ammonolysis Condensation Hydrohalogenation	Ethylene oxide Trimethyl amine
49.	Chloral	None	Halogenation	Acetaldehyde
50.	Chloroacetic Acid	None	Halogenation	Acetic acid
51.	Chlorobenzene (mono)	None	Halogenation	Benzene
52.	*p*-Chlorobenzene Sulfonamide	None	Amination by ammonolysis	*p*-Chlorobenzene sulfonyl chloride
53.	*p*-chloro-*m*-cresol	None	Halogenation	*m*-Cresol
54.	Chloroform	Chloromethanes	Halogenation	Methane
	Chloroform	Methyl chloride Methylene chloride	Halogenation	Methanol
55.	Chloronapthalene	None	Halogenation	β-Naphthol

Table 2, continued

	Product	Other Products	Processes	Feedstock
56.	*o*-Chorophenol	*p*-Chlorophenol	Halogenation	Phenol
57.	Chloropicrin	None	Halogenation	Picric acid
58.	Chloroprene	None	Halogenation	Butadiene
59.	Crotonaldehyde	*n*-Butyl alcohol *n*-Butraldehyde	Condensation Hydrogenation	Acetaldehyde
60.	Cumene	None	Alkylation	Benzene Propylene
61.	Cyanuric Acid	Sodium dichloroisocyanurate, Trichloroisocyanuric acid	Halogenation Pyrolysis	Caustic soda Chlorine Urea
	Cyanuric Acid	None	Pyrolysis	Urea
62.	Cyclohexane	None	Hydrogenation	Benzene
63.	Cyclohexanone	None	Dehydrogenation	Cyclohexane-Cyclohexanol mixtures
	Cyclohexanone	Cyclohexyl Alcohol	Oxidation	Cyclohexane
64.	Cyclohexyl alcohol	None	Hydrogenation	Phenol
	Cyclohexyl alcohol	Cyclohexanone	Oxidation	Cyclohexane
65.	Cyclohexylamine	None	Hydrogenation	Aniline
	Cyclohexylamine	None	Hydrogenation	Nitrobenzene
66.	Di-*n*-butyl phthalate	None	Esterification	*n*-Butyl alcohol, Phthalic anhydride
67.	*m*-Dichlorobenzene	None	Acid rearrangement	Dichlorobenzenes
	m-Cichlorobenzene	None	Halogenation	Benzene
68.	*o*-Dichlorobenzene	*p*-Dichlorobenzene	Halogenation	Benzene

Table 2, continued

	Product	Other Products	Processes	Feedstock
69.	3,3'-Dichlorobenzidine dihydrochloride	None	Benzidine rearrangement, Amination by reduction	1-Chloro-2-nitrobenzene
70.	Dichlorodiphenyl-trichloroethane (DDT)	None	Condensation Halogenation	Acetaldehyde Monochlorobenzene
71.	Dichlorophenol	None	Halogenation	4-Chlorophenol, Phenol
72.	2,4-Dichlorophenoxy acetic acid (2,4-D)	None	Condensation Halogenation	Monochloroacetic acid Phenol
73.	2-(2,4-Dichlorophenoxy) propionic acid (2,4-DP)	None	Condensation Dehydrohalogenation	α-Chloropropionic acid 2,4-Dichlorophenol
74.	4,4'-Dichlorophenylsulfone	None	Condensation	Monochlorobenzene Sulfur trioxide
75.	1,2-Dichloropropane	None	Halogenation	Propylene
76.	1,3-Dichloropropane	None	Halogenation	Allyl chloride
77.	Diethyl Phthalate	None	Esterification	Ethyl alcohol, Phthalic anhydride
78.	Diheptyl Phthalate	None	Esterification	Heptyl alcohol, Phthalic anhydride
79.	Diisodecyl Phthalate	None	Esterification	Isodecyl alcohol, Phthalic anhydride
80.	Dimethylformamide	None	Amination by ammonolysis	Dimethylamine, Methyl formate
81.	Dimethyl Phthalate	None	Esterification	Methyl alcohol, Phthalic anhydride

Table 2, continued

	Product	Other Products	Processes	Feedstock
82.	Dimethyl Terephthalate	None	Esterification	Methyl alcohol, Terephthalic acid
	Dimethyl Terephthalate	None	Esterification Oxidation	Methyl alcohol *p*-Xylene
83.	4,6-Dinitro--cresol	None	Nitration	Cresol
84.	2,4-Dinitrophenol	None	Nitration	Phenol
85.	2,4-Dinitrotoluene	None	Nitration	Toluene
	2,4-Dinitrotoluene	2,6-Dinitrotoluene	Nitration	Toluene
86.	Di-*n*-octyl Phthalate	None	Esterification	*n*-Octyl alcohol Phthalic anhydride
87.	Dioctyl Phthalate (2-ethylhexyl phthalate)	None	Esterification	2-Ethylhexyl alcohol Phthalic anhydride
88.	Diphenylamine	None	Condensation	Aniline
89.	Diphenylguanidine	None	Condensation	Aniline Cyanic acid
90.	N,N'-Diphenylhydrazine (hydrazobenzene)	None	Condensation Hydrogenation	Nitrobenzene
91.	Diphenylmethane-4,4'-diisocyanate (MDI)	None	Phosgenation	Aniline, Formaldehyde, Phosgene
92.	Dodecanoic Acid	Suberic acid	Oxidation Ozonolysis	Cylcic olefins
93.	Dodecene, Nonlinear (propylene tetramer)	None	Polymerization	Propylene

Table 2, continued

	Product	Other Products	Processes	Feedstock
94.	Epichlorohydrin	None	Chlorohydrination Hydrolysis	Allyl chloride Hypochlorous acid
95.	Epoxy Resins	None	Polymerization	Bisphenol A, Epichlorohydrin
96.	Ethanolamines	None	Amination by aminolysis	Ethylene oxide
97.	Ethoxysulfates	None	Sulfonation	Ethoxylates, Sulfur trioxide
98.	Ethyl Acetate	None	Condensation	Acetaldehyde
	Ethyl Acetate	None	Esterification	Acetic acid, Ethyl alcohol
99.	Ethyl Acetoacetate	None	Esterification Pyrolysis	Acetic acid Ethyl alcohol
100.	Ethyl Acrylate	None	Carbonylation (oxo)	Acetylene, Ethyl alcohol Carbon monoxide
	Ethyl Acrylate	None	Esterification Oxidation	Ethyl alcohol, Propylene
101.	Ethyl Alcohol	None	Hydrolysis	Ethylene
	Ethyl Alcohol	Ethyl ether	Hydrolysis	Ethylene
102.	Ethylamines	None	Amination by ammonolysis	Ethanol
103.	Ethyl Benzene	None	Alkylation	Benzene, Ethylene
104.	Ethyl Chloride	None	Hydrohalogenation	Ethylene
105.	Ethylene	None	Dehydration	Ethyl alcohol
	Ethylene	Propylene Hydrogen Pyrolysis gasoline	Pyrolysis	Butanes, or Ethane, or Gas oil, or Naphtha, or Propane
106.	Ethylene Carbonate	None	Condensation	Ethylene oxide, Carbon dioxide
107.	Ethylenediamine	None	Amination by ammonolysis	Ethylene dichloride
	Ethylenediamine	None	Amination by ammonolysis	Monoethanolamine

Table 2, continued

Product	Other Products	Processes	Feedstock
108. Ethylene Dibromide	None	Halogenation	Ethylene
109. Ethylene Dichloride	None	Halogenation	Ethylene
Ethylene Dichloride	None	Oxyhalogenation	Ethylene, Hydrogen chloride
110. Ethylene Glycol	Ethylene oxide	Oxidation	Ethylene
111. Ethylene Glycol Ethers	None	Condensation	Alkyl alcohols, Ethylene glycol
112. Ethylene Glycol Monomethyl Ether	None	Condensation	Ethylene oxide, Ethanol
113. Ethylene Oxide	None	Oxidation	Ethylene
Ethylene Oxide	Ethylene glycol	Hydrolysis Oxidation	Ethylene
114. Ethylene-Propylene Copolymers (EPM)	None	Polymerization	Ethylene, propylene
115. Ethylene-Propylene Terpolymer (EPT)	None	Polymerization	Ethylene, Propylene
116. Ethylene-Vinyl Acetate Copolymer Resins	None	Polymerization	Ethylene, Vinyl acetate
117. Ethyl Ether	None	Condensation	Ethyl alcohol
118. 2-Ethyl Hexanol	None	Condensation Hydrogenation	Acetaldehyde Butyraldehyde
2-Ethyl Hexanol	n-Butyl alcohol Isobutyraldehyde Isobutyl alcohol	Carbonylation (oxo) Hydrogenation	Propylene Carbon monoxide

Table 2, continued

	Product	Other Products	Processes	Feedstock
119.	Ethyl Parathion	None	Condensation Halogenation	0,0-Dimethyl Phosphonothionochloridate Sodium nitrophenoxide
120.	Fluorocarbons	None	Halogenation	Carbon tetrachloride Hydrofluoric acid
	Fluorocarbons	None	Halogenation	Methane, Hydrofluoric acid
121.	Formic Acid	Sodium formate	Carbonylation (oxo) Hydrolysis	Carbon monoxide Sodium hydroxide
	Formic Acid	None	Carbonylation (oxo) Condensation Hydrolysis	Carbon monoxide (methanol recycled)
122.	Formaldehyde	None	Oxidation[a]	Methanol
	Formaldehyde	None	Oxidation[b]	Methanol
	Formaldehyde	None	Oxidation[b]	Dimethyl ether
123.	Formic Acid	None	Oxidation	Light hydrocarbons
124.	Fumaric Acid	None	Isomerization	Maleic anhydride
	Fumraic Acid	None	Isomerization Oxidation	Benzene
125.	Glycerine	None	Chlorohydrination Halogenation Hydrolysis	Propylene→allyl chloride→ epichlorohydrin
	Glycerine	None	Epoxidation Hydrolysis	Allyl alcohol Peracetic acid
	Glycerine	None	Oxidation	Propylene
126.	Heptenes	None	Condensation	Butylenes, Propylene
127.	Hexachlorobenzene	None	Halogenation	Benzene
128.	Hexachlorobutadiene	None	Halogenation	Butadiene
129.	Hexachlorocyclopentadiene	None	Pyrolysis	Pentane

Table 2, continued

	Product	Other Products	Processes	Feedstock
130.	Hexachloroethane	None	Halogenation	Tetrachloroethane
131.	Hexamethylenediamine	None	Amination by ammonolysis	Adipic acid
	Hexamethylenediamine	None	Ammoxidation	Adipic acid
	Hexamethylenediamine	None	Hydrogenation	Adiponitrile
132.	Hexamethylenetetramine	None	Amination by ammonolysis Condensation	Ammonia Formaldehyde
90.	Hydrazobenzene[c] (N,N'-diphenylhydrazine)	None	Condensation Hydrogenation	Nitrobenzene
133.	Hydrogen Cyanide	None	Ammoxidation	Methane
134.	3-Hydroxy-2-Naphthoic Acid	None	Carboxylation	β-Napthol, Carbon dioxide
135.	α-Isoamylene	None	Dehydrogenation	Isopentane
136.	Isobutyl Alcohol	n-Butyl alcohol 2-Ethyl hexanol Isobutyraldehyde	Carbonylation (oxo) Hydrogenation	Propylene Carbon Monoxide
	Isobutyl Alcohol	None	Carbonylation (oxo) Hydrogenation	Propylene Carbon Monoxide
137.	Isobutylene	None	Cracking (catalytic)	Isobutane
138.	Isobutyraldehyde	-Butyl alcohol Isobutyl alcohol 2-Ethyl hexanol	Carbonylation (oxo) Hydrogenation	Propylene Carbon monoxide
139.	Isophthalic Acid	None	Oxidation	m-Xylene
140.	Isophthalonitrile	None	Ammoxidation	m-Xylene
141.	Isophorone	None	Condensation	Acetone

Table 2, continued

Product	Other Products	Processes	Feedstock
142. Isoprene	None	Condensation Cracking (catalytic)	Propylene
Isoprene	None	Condensation Dehydration Hydrogenation	Acetone Acetylene
Isoprene	None	Condensation Cracking (catalytic)	Formaldehyde Isobutylene
Isoprene	None	Condensation Hydrohalogenation Pyrolysis	Formaldehyde Isobutylene Hydrogen chloride
Isoprene	None	Dehydrogenation	*tert*-Amylenes
Isoprene	None	Cracking (catalytic)	Amylenes
Isoprene	None	Dehydrogenation	Isopentane
143. Isopropyl Acetate	None	Esterification	Acetic acid, Isopropyl alcohol
Isopropyl Alcohol	None	Hydrolysis Sulfonation	Propylene
Isopropyl Alcohol	None	Hydrolysis^d	Propylene
144. N-Isopropyl-N'-phenyl-*p*-phenylenediamine	None	Alkylation^e Dehydrohalogenation Hydrogenation	Acetone Aniline *p*-Chloro-nitrobenzene
145. Ketene Dimer	None	Pyrolysis	Acetic acid
146. Lead Alkyls	None	Alkylation	Ethyl chloride, Alkyl chlorides
147. Maleic Acid	None	Hydrolysis	Maleic anhydride
148. Maleic Anhydride	None	Oxidation	Butadiene (plus other C_4 hydrocarbons)
Maleic Anhydride	None	Oxidation	Benzene
Maleic Anhydride	None	Oxidation	Butene-1, Butene-2, Butadiene (if present)
149. Melamine	None	Condensation Pyrolysis	Dicyandiamide
Melamine	None	Condensation Pyrolysis	Urea
150. Mesityl Oxide	None	Condensation Dehydration	Acetone

Table 2, continued

Product	Other Products	Processes	Feedstock
151. DL-Methionine	None	Condensation Hydrogenation	Acrolein Cyanic acid Methyl mercaptan
152. Methyl Acetate	None	Esterification	Acetic acid Methyl alcohol
153. Methyl Acetoacetate	None	Esterification Pyrolysis	Acetic acid Isopropyl alcohol
154. Methyl Alcohol	None	Reforming (steam)[f]	Naphtha
Methyl Alcohol	None	Reforming (steam)[f]	Natural gas
Methyl Alcohol	None	Reforming (steam)[g]	Naphtha
Methyl Alcohol	None	Reforming (steam)[g]	Natural gas
Methyl Alcohol	None	Reforming (steam)[g]	Liquefied petroleum gas
Methyl Alcohol	Methyl ether	Reforming (steam)[g]	Naphtha, Carbon dioxide
155. Methylamines	None	Amination by ammonolysis	Methanol, Ammonia
156. Methyl Bromide	None	Hydrohalogenation	Methanol
157. 2-Methyl-1-butanol (*tert*-amyl alcohol)	None	Condensation Hydrogenation	Acetone Acetylene
158. 2-Methyl-3-butyn-2-ol	None	Condensation	Acetone, Acetylene
159. Methyl Chloride	None	Halogenation	Methanol
Methyl Chloride	None	Halogenation	Methane
Methyl Chloride	None	Hydrohalogenation	Methanol
160. 2-Methyl-4-chloro-phenoxyacetic Acid (MCPA)	None	Condensation Halogenation	*o*-Cresol Monochloroacetic acid
161. 2-(2-Methyl-4-chlorophenoxy) propionic Acid (MCPP)	None	Condensation Dehydrohalogenation	α-Chloropropionic acid, 4-Chloro-*o*-cresol

Table 2, continued

Product	Other Products	Processes	Feedstock
162. Methylene Chloride	Chloroform Methyl chloride	Halogenation	Methyl alcohol
Methylene Chloride	Chloroform Methyl chloride	Halogenation	Methane
Methylene Chloride	Chloroform Methyl chloride	Halogenation	Methane and Methyl alcohol
163. Methyl Ether	Methyl alcohol	Reforming (steam)	Naphtha
164. Methyl Ethyl Ketone	None	Dehydrogenation Hydrolysis	Butene-1 Butene-2
Methyl Ethyl Ketone	None	Dehydrogenation	*sec*-Butyl alcohol
165. 2-Methyl-5-ethyl pyridine (MEP)	None	Amination by amminolysis Condensation	Acetaldehyde Ammonia
166. Methyl Isobutyl Ketone	None	Condensation Dehydration	Acetone Hydrogen
167. Methyl Methacrylate Monomer	None	Esterification Hydrocyanation Hydrolysis Sulfonation	Acetone Hydrogen cyanide Methyl alcohol
Methyl Methacrylate Monomer	None	Esterification Oxidation	Isobutylene Methyl alcohol
168. Methyl Parathion	None	Condensation Halogenation	O,O-Dimethyl phosphorothionochloridate, Sodium *n*-nitrophenoxide
169. 4-Methyl-1-pentene	None	Condensation	Propylene
170. Monochloroacetic Acid	None	Halogenation	Acetic acid
171. Morpholine	None	Dehydration	Diethanolamine
172. Naphthalene	None	Pyrolysis	Coal tar or Petroleum
Naphthalene	None	Hydrodealkylation	Alkyl naphthalenes

Table 2, continued

Product	Other Products	Processes	Feedstock
173. 2-Naphthol	None	Hydrolysis Sulfonation	Naphthalene
174. Nitrobenzene	None	Nitration	Benzene
175. *o*-Nitrophenol	None	Nitration	Phenol
176. *p*-Nitrophenol	None	Nitration	Phenol
177. *m*-Nitrotoluene	None	Nitration	Toluene
178. *o*-Nitrotoluene	None	Nitration	Toluene
179. *p*-Nitrotoluene	None	Nitration	Toluene
180. *p*-Nonyl Phenol	None	Alkylation	Phenol Propylene trimer
181. Oxalic Acid	None	Condensation Pyrolysis	Sodium formate
182. *p*-Oxybenzoic Acid	*p*-Oxybenzoic butyrate	Carboxylation Esterification	Butyl alcohol Carbon dioxide, Phenol
183. Pelargonic Acid	Azeliac acid Caproic acid	Oxidation Ozonolysis	Oils (tall, red soya bean)
Pelargonic	Undecanoic acid Tridecanoic acid	Oxidation Ozonolysis	Alpha-Olefins
184. Pentachlorophenol	None	Halogenation	Phenol
Pentachlorophenol	None	Hydrolysis	Hexachlorobenzene
185. Pentaerythritol	None	Cannizzaro Reaction Condensation	Acetaldehyde Formaldehyde
186. Perchloroethylene	Trichloroethylene	Cracking (catalytic) Halogenation	Ethylene dichloride
Perchloroethylene	Trichloroethylene	Cracking (catalytic) Halogenation	Acetylene
Perchloroethylene	Trichloroethylene	Cracking (catalytic) Halogenation Oxyhalogenation	Any C_2 chlorocarbon mixture

Table 2, continued

Product	Other Products	Processes	Feedstock
187. Phenol	Acetone	Acid cleavage Alkylation Hydrolysis Oxidation	Benzene, Propylene
Phenol	Acetone	Acid cleavage Oxidation	Cumene
Phenol	Hydrogen	Dehydrogenation Oxidation	Cyclohexane
Phenol	None	Hydrolysis	Monochlorobenzene
Phenol	None	Hydrolysis Sulfonation	Benzene, Sulfuric acid
Phenol	None	Hydrolysis Oxyhalogenation	Benzene Hydrogen chloride
188. Phenothiazine	None	Pyrolysis	Diphenylamine, Sulfur
189. N-phenyl-2-naphthylamine	None	Condensation	Aniline, 2-naphthol
190. *p*-Phenylphenol	None	Condensation Dehydrogenation	Benzene, Cyclohexanone
191. Phosgene	None	Halogenatin	Carbon monoxide, Chlorine
192. Phthalic Anhydride	None	Oxidation	Naphthalene
Phthalic Anhydride	None	Oxidation	*o*-Xylene
193. Phthalonitrile	None	Ammoxidation	*o*-Xylene
194. β-Picoline	Pyridine	Ammoxidation Condensation	Acetaldehyde Formaldehyde, Methanol
195. Piperylene	None	Dehydrogenation	*n*-Pentene
196. Polyamide Resins (nylon 6)	None	Polymerization	Caprolactam
197. Polyamide Resins (nylon 66)	None	Polymerization	Adipic acid, Hexamethylene diamine

Table 2, continued

	Product	Other Products	Processes	Feedstock
198.	*cis*-1,4-Polybutadiene[h]	None	Polymerization	Butadiene
199.	Polybutadiene[i]	None	Polymerization	Butadiene
	Polybutadiene[h]	None	Polymerization	Butadiene
200.	Polybutadiene-Acrylonitrile (NBR)[i]	None	Polymerization	Acrylonitrile Butadiene
201.	Polybutadiene (epoxidized)	None	Epoxidation	Acetic acid, Hydrogen peroxide, Polybutadiene
202.	Polybutenes	None	Polymerization	Butene-1, Butene-2
203.	Polycarbonate Resins	None	Dehydrohalogenation Phosgenation Polymerization	Bisphenol-A, Phosgene
204.	Polychloroprene	None	Polymerization	Chloroprene
205.	Polyester Resins (saturated)	None	Polymerization	Glycols, Polybasic acids, Styrene
206.	Polyester Resins (unsaturated)	None	Polymerization	Glycols, Styrene, Unsaturated dibasic acids
207.	Polyether Glycols	None	Polymerization	Ethylene oxide, Propylene oxide
	Polyether Glycols	None	Polymerization	Alcohols, Ethylene oxide, Propylene oxide
208.	Polyethylene (low-density)	None	Polymerization	Ethylene
209.	Polyethylene (high-density)	None	Polymerization	Ethylene
210.	Polyethylene Terephthalate	None	Condensation Polymerization	Dimethyl terephthalate, Ethylene glycol

Table 2, continued

Product	Other Products	Processes	Feedstock
Polyethylene Terephthalate	None	Esterification Polymerization	Ethylene glycol, Terephthalic acid
211. Polyisobutylene	None	Polymerization	Isobutylene, Butenes
212. Polyisocyanate	None	Polymerization Pyrolysis	Organic dichlorides Sodium cyanate
213. cis-Polyisoprene (IR)[j]	None	Polymerization	Isoprene
214. Polypropylene	None	Polymerization	Propylene
215. Polystyrene	None	Polymerization	Styrene
216. Polystyrene (high-impact rubber modified)[l]	None	Polymerization	Polybutadiene, Styrene
217. Polyvinyl Acetate	None	Polymerization	Vinyl acetate
218. Polyvinyl Alcohol Resins	None	Polymerization	Vinyl alcohol
219. Polyvinyl Chloride Resins	None	Polymerization	Vinyl chloride
220. Polyvinyl Chloride-acetate Copolymer	None	Polymerization	Vinyl acetate, Vinyl chloride
221. Polyvinyl Chloride-Vinylidene Chloride Resins	None	Polymerization	Vinyl chloride Vinylidene chloride
222. β-Propiolactone	None	Polymerization	Formaldehyde, Ketene
223. Propylene	None	Dehydrogenation	Propane
Propylene	None	Pyrolysis	Butane, or Gas oils, or Naphtha, or Propane
224. Propylene Carbonate	None	Condensation	Carbon dioxide Propylene oxide

Table 2, continued

Product	Other Products	Processes	Feedstock
225. Propylene Glycol	None	Hydrolysis	Propylene oxide
226. Propylene Oxide	None	Chlorohydrination Halogenation Hydrolysis	Propylene Chlorine solution *tert*-Butyl alcohol (recycled)
Propylene Oxide	Acetic acid	Epoxidation	Propylene 30% Peracetic acid 10-15% Acetic acid
Propylene Oxide	None	Chlorhydrination Hydrolysis	Propylene Chlorine solution Milk of lime
(93.) Propylene Tetramer[k] (Dodecene)	None	Polymerization	Propylene
227. Pyridine	β-Picoline	Ammoxidation Condensation	Acetaldehyde Formaldehyde Methanol
228. Pyromellitic Dianhydride	None	Alkylation Oxidation	1,2,4-Trimethylbenzene (pseudocumene)
229. Salicylic Acid	None	Carboxylation	Phenol, Carbon dioxide, Caustic soda
230. SBR (polybutadiene-styrene)[i]	None	Polymerization	Butadiene, Styrene
SBR (polybutadiene-styrene)[h]	None	Polymerization	Butadiene, Styrene
231. Sodium *p*-aminosalicylate	None	Carboxylation	*m*-Aminophenol, Carbon dioxide, Caustic soda
232. Sodium Formate	None	Carbonylation (oxo)	Carbon monoxide, Sodium hydroxide
233. Sorbitol	None	Hydrogenation	Corn sugar or Corn Syrup
234. Styrene	None	Alkylation Dehydrogenation	Benzen, Ethylene
Styrene	None	Dehydrogenation	Ethylbenzene

Table 2, continued

Product	Other Products	Processes	Feedstock
235. Suberic Acid	Dodecanoic acid	Oxidation Ozonolysis	Cylcic olefins
236. Terephthalic Acid	None	Oxidation	p-Xylene
237. Terephthalonitrile	None	Ammoxidation	p-Xylene
238. 1,1,2,2-Tetrachloroethane	None	Halogenation	Ethane
239. Tetrahydrofuran, 2,3,4,5-Tetracarboxyclic dianhydride	None	Condensation Oxidation	Furan, Maleic anhydride
240. Tetramethylthiuram Disulfide (Thiram)	None	Condensation Oxidation	Ammonia, Carbon disulfide, Dimethylamine, Hydrogen peroxide
241. Toluene Diisocyanate (TDI) (80/20-2,4-2,6-TDI)	None	Hydrogenation Nitration Phosgenation	Phosgene Toluene
242. Triacetin Polymer	None	Esterification	Acetic acid, Cellulose
243. Triacetin (glyceryl tributyrate)	None	Esterification	n-Butyric acid, Glycerol
244. 1,2,4-Trichlorobenzene	None	Halogenation	1,2-Dichlorobenzene
245. 1,1,1-Trichloroethane	None	Halogenation	Ethylene
1,1,1-Trichloroethane	None	Halogenation Hydrohalogenation	Vinyl chloride
246. 1,1,2-Trichloroethane	None	Halogenation	Ethylene
247. Trichloroethylene	Perchloroethylene	Cracking (catalytic) Halogenation	Ethylene dichloride

Table 2, continued

	Product	Other Products	Processes	Feedstock
	Trichloroethylene	Perchloroethylene	Cracking (catalytic) Halogenation	Acetylene
	Trichloroethylene	Perchloroethylene	Cracking (catalytic) Halogenation Oxyhalogenation	Any C_2 chlorocarbon mixture
248.	2,4,5-Trichlorophenol	None	Halogenation Hydrolysis	Benzene Methanol Sodium hydroxide
249.	2,4,5-Trichlorophenoxy-acetic Acid (2,4,5-T)	None	Condensation Halogenation	Acetic acid Trichlorophenol
250.	Tridecanoic Acid	Pelargonic acid Undecanoic acid	Oxidation Ozonolysis	α-Olefins
251.	Trimellitic Anhydride	None	Oxidation	Pseudocumene
252.	Undecanoic Acid	Pelargonic acid Tridecanoic acid	Oxidation Ozonolysis	-Olefins
253.	Urea	None	Amination by ammonolysis Dehydration	Carbon dioxide
254.	Urea-Formaldehyde Resins	None	Polymerization	Biuret, Formaldehyde, Urea
255.	Vinyl Acetate	None	Hydroacetylation	Acetylene Acetic acid
	Vinyl Acetate	None	Oxyacetylation	Ethylene, Acetic acid, Oxygen
256.	Vinyl Chloride Monomer (VCM)	Hydrogen chloride	Dehydrohalogenation	Ethylene dichloride
	Vinyl Chloride Monomer (VCM)	None	Dehydrohalogenation Halogenation Oxyhalogenation	Ethylene Chlorine
	Vinyl Chloride Monomer (VCM)	None	Dehydrohalogenation Halogenation Oxyhalogenation	Ethane Chlorine

Table 2, continued

Product	Other Products	Processes	Feedstock
Vinyl Chloride Monomer (VCM)	None	Dehydrohalogenation Halogenation	Acetylene Chlorine
Vinyl Chloride Monomer (VCM)	None	Dehydrohalogenation Halogenation Oxyhalogenation	Naphtha Chlorine
Vinyl Chloride Monomer (VCM)	None	Hydrohalogenation	Acetylene, Chlorine
257. Vinylidene Chloride	None	Dehydrohalogenation Halogenation	Vinyl chloride Chlorine
258. o-Xylene[l]	p-Xylene	Isomerization	Aromatic mixtures
o-Xylene[m]	p-Xylene	Isomerization	Xylenes, mixed
o-Xylene[n]	p-Xylene	Isomerization	Xylenes, mixed
259. Xylenes, mixed	--	Dehydrogenation	Naphtha
260. m-Xylenediamine	None	Hydrogenation	Isophthalonitrile
261. 2,4-Xylenol	None	Alkylation	p-Cresol, Methyl chloride
262. Zineb	None	Condensation	Carbon disulfide, Ethylenediamine, Zinc sulfate
263. Ziram	None	Condensation	Carbon disulfide, Ethylenediamine, Zinc sulfate

[a] Silver catalyst.
[b] Metal oxide catalyst.
[c] Listed under N,N'-diphenylhydrazine as No. 90.
[d] Direct catalytic hydrolysis.
[e] Reductive alkylation.
[f] High pressure.
[g] Low pressure.
[h] Solution polymerization.
[i] Emulsion polymerization.
[j] Suspension polymerization.
[k] Listed under Dodecene as No. 93.
[l] Catalytic isomerization.
[m] Catalytic isomerization with $HF-BF_3$.
[n] Catalytic isomerization with nonnoble metal.

Source: Herrick, et al., 1979

2.2 REVIEWING THE PREMANUFACTURING NOTICE

The second step of the methodology is to review the submitted PMN. A premanufacturing notice (PMN) is submitted to the U.S. Environmental Protection Agency (EPA), by the interested party at least 90 days before manufacturing of a new chemical is scheduled. This section is divided into three parts. First, the responsibilities of the EPA required by Section 5 of TSCA will be presented. Second, the responsibilities of the private sector are discussed, i.e., the information they are required to provide to the EPA under Section 8 of TSCA. Third, information in the PMN that can be used to estimate emissions during manufacture of the new chemical is discussed.

2.2.1 TSCA Section 5 Requirements

Section 5 of TSCA indicates when a PMN should be submitted to the EPA by the private sector and what detailed information the EPA should consider before arriving at a decision on the production of the new chemical. Within 90 days, the EPA must determine whether the new chemical can be manufactured and used in the proposed manner without causing any harmful effects. According to Section 5 of TSCA, the EPA can arrive at a decision after considering the following factors:

> *(a) "The projected volume of manufacturing and processing of a chemical substance,*
>
> *(b) The extent to which a use changes the type or form of exposure of human beings or the environment to a chemical substance,*

(c) *The extent to which a use increases the magnitude and duration of exposure of human beings or the environment to a chemical substance, and*

(d) *The reasonably anticipated manner and methods of manufacturing, processing, distribution in commerce, and disposal of a chemical substance."*

A PMN is not required under Section 8 of TSCA to provide sufficient information to enable the above 4 factors to readily form part of the decision-making process. If items a, b, c, and d are not addressed appropriately in the submitted PMN, then the EPA may call the company and ask for more information. However, since the information is not officially required, the EPA only calls when they feel that information is absolutely necessary (personal communication with Mary Cushmak[1]). The EPA will often try to answer items a, b, c, and d using the information provided and engineering and other analyses.

2.2.2 TSCA Section 8 Requirements

Section 8 of TSCA lists the information that is required of the private sector when submitting a PMN:

(e) *"The common or trade name, the chemical identity, and the molecular structure of each chemical substance or mixture for which such a report is required,*

(f) *The categories or proposed categories of use of each such substance or mixture,*

(g) *The total amount of each such substance and mixture manufactured or processed, reasonable estimates of the total amount to be manufactured or processed, the amount manufactured or processed for each of its categories of use, and reasonable estimates of the amount to be manufactured or processed for each of its categories of use,*

(h) *A description of the by-products resulting from the manufacture, processing, use, or disposal of each such substance or mixture [amounts are not required],*

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[1] Personal communication between Mary Cushmak, USEPA, and Kate Richter, Versar Inc., on October

(i) *All existing data concerning the environmental and health effects of such substance or mixture,*

(j) *The number of individuals exposed, and reasonable estimates of the number who will be exposed, to such substance or mixture in their places of employment and the duration of such exposure [amounts/composition/location are not required],*

(k) *In the initial report on such substance or mixture, the manner or method of its disposal, and in any subsequent report on such substance or mixture, any change in such manner or method."*

Since these factors are required by law, if they are not included in the PMN, the EPA will return the PMN to the company and ask that these factors be addressed.

It is clear that a discrepancy exists between what is actually required to be submitted on a PMN and the information the EPA must review in order to make a decision. Another complication is that the proposed form for a PMN in the Federal Register thoroughly covers the production and use of a new chemical. Upon using this form, a company may supply all the detailed information to satisfy factors a through d or just answer the minimum requirements, e through k. Therefore, the data supplied in PMNs varies from only enough data to fulfill the basic requirements to data providing a total assessment of the chemical. For our use in estimating emissions during manufacture of a new chemical, the more information supplied, the more accurate the estimations will be.

2.2.3 Information Needed to Estimate Emissions During PMN Manufacture

Table 3 shows the information needed from a PMN to use this methodology for estimating emissions during manufacture. This table shows whether these pieces of information needed are required by TSCA and how they can be obtained if not given. The single most important piece of data, that is not specifically itemized in factors e thorough k but that is needed by the EPA, is the process flow diagram. This methodology for estimating emissions requires a process flow diagram. If a flow diagram is not provided with the PMN, we suggest calling the company and requesting it. Engineering estimates can not be expected to describe the process as accurately as the flow diagram.

TABLE 3. INFORMATION NEEDED TO ESTIMATE EMISSIONS DURING PMN MANUFACTURE

Information Needed	Required[a]	How to Obtain
Physical/chemical properties of all components		
Chemical identity, chemical structure	e	
Phase at room temperature	e	Usually given in PMN or CEER Report[b]
Boiling point	NR	CEER Report[b]
Melting point	NR	CEER Report[b]
Vapor pressure	NR	CEER Report[b]
Solubility in water	NR	CEER Report[b]
Phase during reaction	NR	Must be estimated by reviewing process diagram (see Section 2.3)
Chemical reaction occurring	g	Usually given in PMN. See IRC Report[c]
High or low pressure reaction/process	NR	See Section 2.3 of this report
High or low temperature reaction/process	NR	See Section 2.3 of this report
Catalytic reaction	NR	Usually given with chemical reaction description
Product impurities	h	Given but quantity is not required. See IRC Report[c]
By-product from manufacture	h	Given but quantity is not required. See IRC Report[c]
Production volume	g	
Process information		
Block Diagram	NR-d	This is necessary; we suggest calling the company and obtaining it or see ER Report[d]
Mass balance	NR-d	If a block diagram is supplied, a mass balance is usually supplied. Also see ER Report[d]
Location/composition of environmental releases	NR-c	Can be reasonably estimated from block diagram, mass balance and estimating emissions methodology and ER Report[d]
Number of individuals exposed and duration	j	The amount exposed to is not required Specific employee location in the plant is not required
Method of disposal	k	See ER Report[d]
Proposed pollution control equipment	NR	Generally given with method of disposal
Storage	NR	Must estimate (see Section 2.6) or call company
Handling (Transportation)	NR-d	Usually given in PMN

[a] e-k: If required, then will designate which requirement - e through k (see Section 2.2.1).
NR: means not required. If a letter (a-d) is following NR, this means it is considered a relevant factor by USEPA in determining if a chemical can be produced and therefore can ask the company to supply this information (see Section 2.2.2).

[b] CEER Reports (Consumer and Environmental Exposure Reports) discussed in Section 2.3 are prepared by the Exposure Assessment Branch, USEPA/OPTS.

[c] IRC Report (Initial Review Chemistry Report) prepared by the Industrial Chemistry Branch USEPA/OPTS; see Section 2.3.

[d] ER Reports (Engineering Review) discussed in Section 2.4 are prepared by the Chemical Engineering Branch, USEPA/OPTS.

For review of the PMN - Table 3 should be used as a checklist. Each item in Table 3 should be addressed. The PMN should be read critically and all data gaps observed. An attempt should be made to fill the PMN data gaps until Table 3 is complete. The confidence of the emissions data decreases with each added estimation on Table 3 .

Much information can be gained from a PMN. The amount of information given on each PMN varies from the basic requirements to a total assessment of the chemical. On a scale of 1 to 10, the basic requirements would rate a 1 and the total assessment would rate a 10. Our preference when using this methodology is to at least collect all the items on Table 3 (rating of a 5 or better). The resulting information would include the chemical reactions involved, a process flow diagram, a mass balance including by-products of the reaction, and methods of disposal including pollution control equipment. From this information, we can evaluate the emissions from each piece of equipment, the storage and handling emissions, and the fugitive emissions.

2.3 CONDUCTING A CHEMISTRY REVIEW

This step of the methodology for estimating environmental releases from PMN manufacture reviews the available information on the PMN chemical which will aid in calculating a materials balance and resultant emissions. In this section, we will conduct a chemistry review of the PMN chemical reaction and mention the importance of the physical state of the reaction in the reactor and its operating conditions. The former step will generate the data needed for a materials balance, and the latter step will yield the type of emissions that are likely to occur from the reactor.

Specifically, we would like to generate the following information from the chemistry review of the PMN chemical:

Chemical identities and structures
Physical state of components at ambient conditions
Vapor pressures
Solubilities in water
Production volume
Amounts or weight or mole percents entered or produced to yield production volume

And also we would like to gain the following chemical reaction information:

Chemical reaction(s) involved
Side reactions(s)
Impurities formed
By-products formed
Percent yield of reaction
Physical state of reaction
Catalyst used, if any
Temperature
Pressure

2.3.1 Physical/Chemical Properties

The physical/chemical properties of the PMN chemicals can be found in the PMN or the CEER reports. The CEER reports, (Consumers and Environmental Exposure Reports) are prepared by the Exposure Assessment Branch, OPTS/USEPA. The physical properties, environmental fate and pathways, and health effects of PMNs are estimated in these reports
The physical properties, for instance, phase at ambient conditions, vapor pressure, and solubility in water of all the other components, should be available in the published literature. For cases where the data are unavailable, estimation techniques for calculating these properties can be obtained from A.D. Little (1981). The CEER reports use these techniques to estimate the properties for the PMN chemicals.

The production volume of the chemical is given in the PMN. The amounts of reactants entering can be determined from a mass balance provided with the PMN or by looking at the reaction stoichiometry. A physical property useful in estimating releases is the feedstock purity. Values for the feedstock impurities, usually by weight percent, can be obtained from industry-related literature or by calling the feedstock producers. For instance, merchant chlorine contains 1 to 3% impurities of CO_2, H_2, and N_2, which are usually emitted to the atmosphere after reaction. As much impurity information as possible should be obtained because feedstock impurities are either released or contribute to side reactions.

2.3.2 Reaction Kinetics and Thermodynamics

The chemical reaction(s) and side reactions involved, impurities formed, and by-products formed are usually given in the PMN or can be obtained from the IRC reports. The Industrial Chemistry Branch, OPTS/USEPA, conducts a "chemical review" on all PMN chemicals, regardless of whether the reactions are offered in the PMN. Their results are issued in an Initial Review Chemistry Report.
For their studies, a chemist reviews related and structurally similar chemicals and their reactions, side reactions, impurities, and percent yields.

The reaction kinetics and thermodynamics, such as the physical state of the reaction, its operating conditions, and catalyst use, are usually hard to determine. These parameters will indicate possible emission points, for instance, whether a reactor off-gas vent is likely or not or whether unwanted liquid streams or solid residues will collect on the bottom of the reactor. Generally, the phase in the reactor is not readily available information, but it can be deduced by looking at the physical state of the reactants and products at ambient conditions and the process flow diagram. For instance, one should note the type equipment that handles gases, liquids, or slurries like absorbers, distillation columns, and centrifuges.

Determining the operating temperature and pressure in the reactor and resulting phase is a complicated heat and mass-transfer, reactor-design problem (see Perry, 1973) and is not part of this methodology. If the operating conditions are specified, the vapor pressure, etc. at that temperature and pressure should be used to develop emissions information; otherwise, it can be ignored.

Catalyst use is also important for estimating releases. One should note whether the reaction requires a catalyst and, if so, whether it is regenerated. Catalysts become a solid waste after their useful life is complete and an organic release to air when they are regenerated.

2.4 CONDUCTING AN ENGINEERING ANALYSIS

The most important piece of engineering data for analyzing emissions of PMN chemicals is the process flow diagram. If a flow diagram is not provided with the PMN, we suggest calling the company and requesting it. Alternatively, an engineering analysis can be performed to obtain a reasonable flow diagram by reviewing patents of similar chemicals and using engineering judgement. However, this is not as accurate as obtaining the actual flow diagram.

The Chemical Engineering Branch, USEPA, produces Engineering Review (ER) Reports as part of the PMN process. These reports review the block diagram when it is provided in the PMN and work out engineering analyses of possible flow diagrams when they are not provided with the PMN. The ER report should be acquired if a flow diagram is not presented in the PMN. Another flow diagram source is the construction permits that companies must submit to the State Air Pollution Control Boards before constructing or modifying a facility. These permits contain the proposed process flow construction or modification and the estimated resultant air emissions when in operation.

Once the PMN process flow diagram has been obtained, qualitative and quantitative data on emissions can be determined by following the methodology described in Section 2.5.

2.5 PROCESS RELEASES

This section is divided into 2 parts: (1) how to use the process flow diagram to identify release points from unit operations and unit processes, and (2) how to quantify the process releases once they have been identified. The outcome of this section will be a materials balance, an indication of where emissions might occur, and a quantification of the large process emissions. Figure 2 illustrates the procedures for quantifying process releases.

2.5.1 Qualitative Analysis of Releases

In this subsection, the environmental release points will be identified by first looking at the ranking of releases of the 23 unit processes and seeing where the PMN chemical manufacturing process ranks, based on its type of unit process. This procedure will then be repeated to identify the unit operations involved in the PMN process and to judge how serious their environmental releases may be. At best, process release ranking is a screening procedure to quickly eliminate processes and equipment which will have small releases.

2.5.1.1 By Unit Process

Step 1 is to classify the PMN chemical manufacturing process according to one or more of the 23 unit processes in the environmental data base in Appendix A. The PMN chemicals can be classified by reviewing the type of reaction(s) involved. Examples are an alkylation reaction or an esterification reaction; it is also possible to have different successive reactions, like a halogenation reaction followed by a condensation reaction.

The next step is to rank the severity of the possible PMN chemicals air emissions based on its process class. Table G-1 ranks the unit processes in decreasing order of air emissions. This table was compiled by

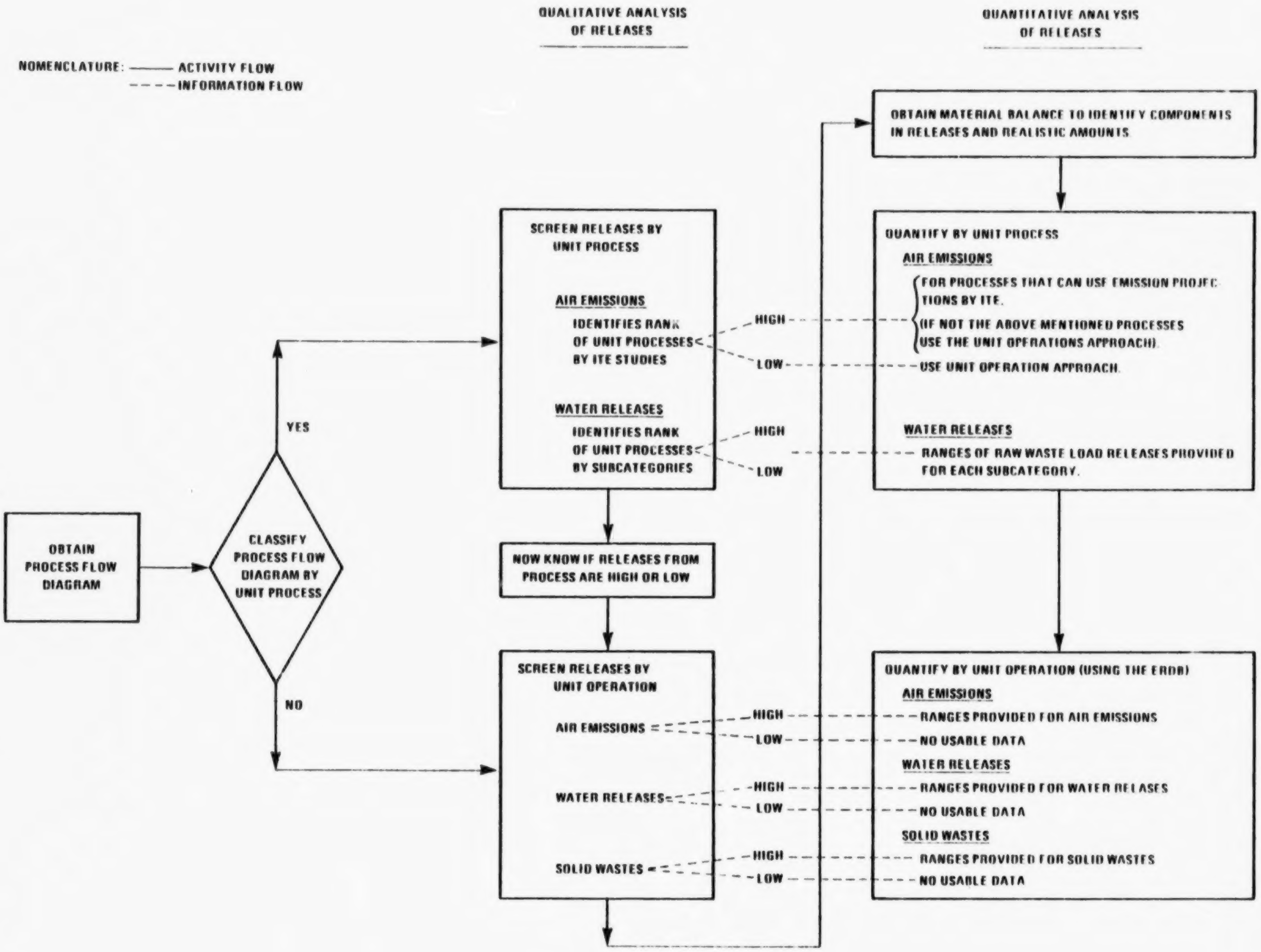
QUALITATIVE ANALYSIS OF RELEASES
QUANTITATIVE ANALYSIS OF RELEASES
NOMENCLATURE: ——— ACTIVITY FLOW
- - - - INFORMATION FLOW
OBTAIN PROCESS FLOW DIAGRAM
CLASSIFY PROCESS FLOW DIAGRAM BY UNIT PROCESS
YES
NO
SCREEN RELEASES BY UNIT PROCESS
AIR EMISSIONS
IDENTIFIES RANK OF UNIT PROCESSES BY ITE STUDIES
WATER RELEASES
IDENTIFIES RANK OF UNIT PROCESSES BY SUBCATEGORIES
HIGH
LOW
HIGH
LOW
NOW KNOW IF RELEASES FROM PROCESS ARE HIGH OR LOW
SCREEN RELEASES BY UNIT OPERATION
AIR EMISSIONS
WATER RELEASES
SOLID WASTES
HIGH
LOW
HIGH
LOW
HIGH
LOW
OBTAIN MATERIAL BALANCE TO IDENTIFY COMPONENTS IN RELEASES AND REALISTIC AMOUNTS
QUANTIFY BY UNIT PROCESS
AIR EMISSIONS
FOR PROCESSES THAT CAN USE EMISSION PROJECTIONS BY ITE.
(IF NOT THE ABOVE MENTIONED PROCESSES USE THE UNIT OPERATIONS APPROACH).
USE UNIT OPERATION APPROACH.
WATER RELEASES
RANGES OF RAW WASTE LOAD RELEASES PROVIDED FOR EACH SUBCATEGORY.
QUANTIFY BY UNIT OPERATION (USING THE ERDB)
AIR EMISSIONS
RANGES PROVIDED FOR AIR EMISSIONS
NO USABLE DATA
WATER RELEASES
RANGES PROVIDED FOR WATER RELEASES
NO USABLE DATA
SOLID WASTES
RANGES PROVIDED FOR SOLID WASTES
NO USABLE DATA

FIGURE 2 QUANTIFICATION PROCEDURE FOR PROCESS RELEASES

White (1980) and will be used as our guide for estimating air emissions. Table C-1 was mainly compiled from release data on process vents. Step 2 is performed by ascertaining where the PMN process class is situated in this table. If it is a two or more unit process chemical, then the most severe rank should be considered. Notice that if the PMN chemical is an oxidation-type reaction or a halogenation type reaction, the air emissions are quite severe.

The third step is to categorize the possible wastewaters from the PMN chemical in the same manner as USEPA (1974a) has categorized the wastewaters from the organic chemicals industry into the 4 subcategories outlined in Table C-2. The 23 unit processes have been put into subcategories A through D as shown in Table C-3. Because of the diversity in unit operations and chemical reactions within each unit process, the unit processes may fall into more than one subcategory. Table C-4 shows the increasing ranges of process water raw waste loads for subcategories A through D. Polymerization reactions have been discussed in more detail by USEPA (1974b) and have been placed in their own subcategories (see Table C-5).

To determine the possible wastewater from the PMN chemical, the PMN chemical should be placed in a subcategory by using Table C-2, C-3, or C-5. Then the range of process raw waste loads released by that subcategory can be pinpointed, using Table C-4. These are the possible raw waste loads of the PMN chemical.

After performing these three steps, one knows how severe the possible air and water releases can be based on the 23 unit processes and also where efforts should be concentrated in estimating releases when reviewing the unit operations.

2.5.1.2 By Unit Operation

Because of the wide variation of behavior within each process class, unit operations must be analyzed in greater detail. This section discusses qualitative gaseous, liquid, and solid releases from different classes of equipment. Tables C-6, C-7, and C-8 list the potential sources of release to air, water, and land from heating and cooling unit operations and product purification and separation unit operations. The releases from reactors are shown in Table C-9. These tables reflect emissions from the average operation of this equipment. The notation "none" does not necessarily mean that there is not potential for release from these unit operations. Fugitive emissions are not mentioned but will occur from all unit operations. Every piece of equipment is periodically cleaned. Cleaning releases are not reflected in these tables, but must be considered. These tables help one to readily discern where emissions are going to occur within the PMN manufacturing process.

Table C-10 lists in decreasing order of equipment air release emissions. Since absorption, scrubbing, and distillation are the unit operations that emit the most air emissions, they are discussed in more detail in Table C-7. Table C-11 lists the major contributing unit operations to wastewater. Table C-12 lists the unit operations which release solid wastes.

Step 4 is to consider each unit operation in the PMN process flow diagram. Potential air, liquid, and solid releases from each unit operation should be listed from Tables C-6 through C-9. The severity of these releases can then be noted from Tables C-10 through C-12 for air, water, and solids.

2.5.2 Quantification of Releases

Releases are quantified in the following manner. The first step is to obtain the materials balance. Second, by referring to the materials balance, air emissions can be estimated for the large air emission unit processes using a method developed by White (1980). And third, all other releases can be found by analyzing each unit operation and the ranges given in Tables C-6 through C-9.

2.5.2.1 Materials Balance

Make an overall manufacturing process mass balance by taking into account the following factors(White 1980):

A. Impurities
  1. Purity of feed
     Impurities contained in reactants
  2. Impurities formed during the reaction

B. Stoichiometry information and excess reactants used

C. Percent yield of reaction

D. By-products
   Exiting stream from reactor including product, unreacted reactants, inerts, and impurities

E. Physical state of all components

F. Vapor pressure and solubility in water of all components (high/low)

Data sources for the mass balance are the PMN and the ER and IRC reports.

To obtain a materials balance, factors A through D should be used to obtain a mass balance around the reactor. Then move to the next piece of separation equipment; estimate its separation efficiencies (which can be obtained in the literature). Use worst case examples. Impurities and by-products must exit somewhere; unless they are reused, they usually end up in the waste streams. Using their physical data, i.e., vapor pressure and solubility in water, and the process flow diagram, possible emission points should be listed. Small amounts of products are also contained in these releases; their points of release should be determined. This procedure will be illustrated in the example in Section 3.

2.5.2.2 Inert-Carrier Gas Method for Estimating Air Emissions

White (1980) has developed the inert-carrier gas method for estimating emissions from those unit processes that release the most air emissions. Two methods using the inert-carrier gas approach have been developed, one for all reactions involving inert-carrier gases and another, a subset of the first, specifically for air-using processes.

2.5.2.2.1 Inert-Carrier Gas Emission Projections

Inert carrier gases can be organic or inorganic gases and can result from the reactants or products of the reaction or from non-reaction related sources. If a component exists as a gas, at the temperature and pressure existing at the emission point, then it is an inert carrier gas. Reaction-related gases can be quantified reactions by reviewing the following factors and placing numbers in the equations in Table C-13.

1. Stoichiometry - see if excess reactants are employed and see if gaseous non-product gases are formed
2. Purity of the reactants
3. The extent of separation of the product and excess reactants
4. The existence of other carrier-gas mechanisms

To explain how to use the equations in Table C-13, a reaction has been selected where one of the reactants is chlorine. These equations can be used for any inert-carrier gas that have all of the required data. This emission projection method analyzes the feed impurities, the excess feed, and the percent yield of the reaction and multiplies these by the separation efficiency of the separation-recovery equipment.

Charts are available in White (1980) which make these calculations very straightforward. The example in Section 3 uses this method for a halogenation reaction.

2.5.2.2.2 Air-Oxidation Emission Projection

The air-oxidation emission projection also uses the inert-carrier gas approach. The carrier gases in oxidation reactions enter with the air, excess oxygen, gases formed during reaction, and nonseparable organics at near atmospheric pressure. Three major factors define the flow of air carrier gases:

1. The chemical oxidation reaction stoichiometry
2. The quantity of product produced
3. The excess air fed to the reactor (design specific from each plant)

Table C-14 presents the equations used in this method. When using air as an oxygen supply one only has to find the variable A, the air-carrier gases, because that variable will be much larger than the other factors. When air is not the source of oxygen supply, then the method described previously should be used. There are charts and examples in White (1980, Vol. 2) which aid in using this method.

These two methods estimate the total gas flow rate and composition that will be emitted as a result of an inert-carrier gas process or an air-using process. These emissions are likely to occur from the reactor off-gas or its absorbers. A large amount of feedstock purity and separation efficiency data are required; if these can be provided then gaseous emissions can be quantified for this type of process. The next section should be used to obtain water and solid releases. All releases from the other unit processes are described in the next section.

2.5.2.3 Quantifying Releases from Ranges of Releases for Unit Operations

In the absence of other methodologies for estimating emissions, one must use the ranges of releases from unit operations that the environmental release data base in Appendix A has provided. These ranges are given in Tables C-6 through C-9 for the unit operations for which there were data. If a unit operation does not have any release information, then either it is a small release or it has not been researched. The reliability of these ranges is explained in Section 2.9.

In order to quantify emissions by using these ranges, every piece of information learned in the qualitative analysis (Section 2.4.2) and the materials balance should be used. Where high and low releases occur and where the by-products and their amounts will be released should be noted. The materials balance will tell the amounts released and the components of the release. For each unit operation, the qualitative information gathered in Section 2.4.2 should be used and a range based on the materials balance or the range already designated should be set up. Where possible, quantifications should be made; this will cover the large process releases. All of these ranges of releases can then be added to obtain an overall range of releases from the PMN process for air, liquid, and solid releases. This methodology is illustrated in the example in Section 3.

2.6 STORAGE AND HANDLING EMISSIONS

This section is divided into two parts: 1) identification of storage and handling requirements and 2) quantification of releases.

2.6.1 Identification of Storage and Handling Requirements

The SOCMI processes have storage and handling requirements for feedstock, intermediate and final products, usable by-products, waste tars, residues and nonusable by-products. The following data sources will be consulted to determine the storage and handling requirements for a given process:

1) Erikson, D.G., September 1980. Storage and Handling. Report 1 of Organic Chemical Manufacturing, Volume 3: Storage, Fugitive and Secondary Sources. Prepared for USEPA/OAQPS/ESED, RTP, NC. EPA-450/3-80-025. Information on SOCMI storage and handling practices on an industry-wide basis.
2) White, R. E., 1980. Organic Chemical Manufacturing. Volumes 6-10 Selected Processes. EPA Report No. EPA-450/3-80-028a-e. Provides useful data on the number of storage vessels used for selected "model" processes.
3) Industry responses to state Emissions Inventory Questionaires (EIQ) particularly in Texas and Louisiana where organic chemicals production is estimated to be 65% of the total SOCMI production. Information is provided only for processes that emit more than 100 tons/year.

2.6.2 Quantification of Releases

Quantification of releases will include emissions from storage and handling.

2.6.2.1 Storage Releases

Storage releases depend on the kind of storage tank in use, e.g., fixed roof, floating roof, or pressure tank. The criteria used for tank selection include material stability and degrees of safety and health hazards but primarily depend on the vapor pressure of the fluid in storage. Table 4 lists the vapor pressure ranges that determine the appropriate tank class plus the use patterns for storage tanks.

Table 5 includes formulae for caluculating the uncontrolled breathing emissions and working losses for fixed roof tanks plus the effects of control technology. Table 6 shows how to calculate standing storage losses and withdrawal losses from floating roof tanks. Pressure vessels are considered to be closed systems with no estimated emissions.

2.6.2.2 Handling Releases

Table 7 includes a formula to calculate loading losses for tank car, tank truck, and marine vessel loading.

2.7 FUGITIVE EMISSIONS

This section is divided into two parts, 1) identification of sources of fugitive emissions and 2) quantification of fugitive releases.

2.7.1 Identification of Sources of Fugitive Releases

The discussion will first cover uncontrolled releases and then deal with controlled releases.

2.7.1.1 Uncontrolled Releases

Erickson and Karcevic (1981) have listed five equipment components as the major sources of uncontrolled fugitive releases in the synthetic

TABLE 4. Selection Criterion and Usage Patterns for Storage Tanks[1]

1. Selection Criterion

Liquid Vapor Pressure KPa (atms)	Tank Selected
0 - 34.5 (.34)	Fixed roof
6.9(.068) - 34.5 (.34)	Floating roof
>51.7 (.51)	Pressure tanks

2. Use Pattern for Storage Tanks

Type Tank	# of Tanks	Percentage of Total Tanks	Percentage of Total Volume Storage Space
Fixed roof	14,800	73%	61%
Floating roof	700	3%	20%
Pressure	4,800	24%	19%

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[1] Reference: Erickson, D.G., September 1980. Storage and Handling, prepared for the USEPA/OAQPS/FSED, Research Triangle Park, North Carolina.

TABLE 5. FORMULA FOR THE CALCULATION OF EMISSIONS FROM FIXED ROOF TANKS[1] FORMULA

Emissions from fixed roof tanks consist of breathing emissions and working losses.

1. Breathing Emissions[2,3]:

where $$L_B = 9.15 \times 10^{-6} \times M \times \left[\left(\frac{P}{14.7-P}\right)^{0.68}\right] \times D^{1.73} \times H^{0.51} \times \Delta T^{0.5} \times F_p \times CK_c \qquad (1)$$

L_B = fixed roof breathing loss (kkg/yr).
M = molecular weight of vapor in storage tank (lb/lb mole).
P = true vapor pressure at bulk liquid conditions (psia).
D = tank diameter (ft).
H = average vapor space height (ft; used 1/2 tank height).
ΔT = average diurnal temperature change (°F; use 20°F).
F_p = paint factor (dimensionless, assuming a white tank in good condition; factor = 1).
C = adjustment factor (dimensionless) for large-diameter tanks ($D \geq 30$ ft), $C = 1$; for small-diameter tanks (less than 30 ft)= $0.0771 (D) - 0.0013 (D^2) - 0.1334$,
K_c = crude-oil factor (dimensionless; use 1.0).

2. Working Losses

The following equation can be applied to all fixed-roof tanks with or without conservation vents:

$$L_W = 1.09 \times 10^{-8} \, MPK_nK_c \, VN, \qquad (2)$$

where

L_W = fixed-roof working loss (kkg/yr).
N = turnovers per year.
K_n = turnover factor (dimensionless)
= $(180 + N)/6N$ for $N > 36$ and $= 1$ for $N \leq 36$.
V = tank volume (gal).
$M, P, \& K_c$ = same as for fixed-roof breathing losses.

3. Effect of Control Technology

Emissions from fixed roof tanks can be reduced from 90 (by adding interval floating covers or a covered floating roof) to 95 percent (using vapor recovery systems such as vapor/liquid absorption, vapor compression, vapor cooling, and vapor/solid adsorption).

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[1] Data Sources: American Petroleum Institute, Evaporation Loss Committee. Evaporation Loss from Fixed Roof Tanks. Bull. 2518. Washington, D. C. 1962; American Petroleum Institute, Division of Refining. Petrochemical Evaporation Loss from Storage Tanks. Bull. 2523, New York, 1969.; Subsequent Modifications in D. G. Ericson, Sept. 1980. Storage and Handling, prepared for USEPA/OAQPS/ESED, Research Triangle Park, North Carolina.

[2] Assumption: No conservation vent is installed in the tank.

[3] Calculated breathing losses may deviate ± 10% from actual breathing loss.

TABLE 6. FORMULAE FOR THE CALCULATION OF EMISSIONS FROM FLOATING ROOF TANKS[2]

Emissions from floating roof tanks consist of standing storage losses and withdrawal losses.

1. Standing Storage Losses[2]

$$L_s = 0.00921\, M\left(\frac{P}{14.7 - P}\right)^{0.7} D^{1.5}\, v_w^{0.7}\, K_t K_s K_p K_c\, \frac{365}{2205} \qquad (3)$$

where

L_s = floating-roof standing storage loss (kkg/yr)

v_w = average wind velocity (miles/hr; use 9.0)

K_t = tank type factor (dimensionless; use 0.045 based on welded tank)

K_s = seal factor (dimensionless; use 1.0)

K_p = paint factor (dimensionless; use 0.9 based on white paint)

M,P,D, and K_c = same as for fixed-roof breathing losses.

2. Withdrawal Losses[3]

$$L_{wd} = 0.000198\, DTHd\, \frac{1}{2205} \qquad (4)$$

where

L_{wd} = floating roof withdrawal loss (Mg/yr)

D = tank diameter (ft)

T = turnovers (per year)

H = tank height (ft)

d = density of stored liquid at bulk liquid conditions (lb/gal)

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[1] Both open-top and internal-floating-roof tanks with single primary seals are covered.

[2] Data Sources: American Petroleum Institute, Evaporation Loss Committee, Evaporation Loss from Floating Roof Tanks. Bull. 2517. Washington, D.C., 1962. American Petroleum Institute, Division of Refining. Petrochemical Evaporation Loss from Storage Tanks. Bull. 2523. New York, 1969. Subsequent Modifications in D. G. Erickson, September 1980. Storage and Handling prepared for USEPA/OAQPS/ESED, Research Triangle Park, North Carolina.

[3] Data Sources: American Petroleum Institute, Evaporation Loss Committee, Evaporation Loss from Low Pressure Tanks. Bull. 2516. Washington, D.C. 1962. Erickson, D. G. op. cit.

TABLE 7. CALCULATION OF LOADING LOSSES[1]

The following equation can be applied to tank-car, tank-truck, and marine-vessel loading and assumes that no supplemental emission control device is in use:

$$L_L = 12.46 \frac{SPM}{T} \frac{V}{1000} \frac{1}{2205} \qquad (5)$$

where

L_L = loading loss (kkg/yr)
S = saturation factor (dimensionless; used 1.0 for tank truck and tank car and 0.2 for marine vessels)
P = true vapor pressure of the liquid loaded (psia)
M = molecular weight of vapors (lb/lb mole)
T = bulk temperature of liquid loading [°R; use 540°R (80°F)]
V = volume loaded (gal/yr)

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[1] Source: C. C. Masser, August 1977. Transportation and Marketing of Petroleum Liquids in Compilation of Air Pollution Emission Factors, AP-42, Part A, 3rd ed., pps 4.4-5 and 4.4-7.

organic chemical manufacturing industry (SOCMI) viz. pumps, valves, compressor seals, flanges, and cooling towers. Further subclassifications were also used. For example, four subcategories were used for pumps depending on the kind of seal used: single mechanical seals, double mechanical seals, packed seals, and sealess.

Fugitive emission factors for SOCMI are considered equivalent to those prevailing in petroleum refining operations for which a rich load of data exists (Wetherold, 1979; Wetherold, 1980). Emissions factors have been grouped depending on whether the process fluid belongs to one of these categories: vapor service, light-liquid service, and heavy liquids service. Table 8 gives the uncontrolled fugitive emission factors for SOCMI.

No data are available on agitator seals or cooling tower emission factors.

2.7.1.2 Controlled Releases

Table 9 highlights the effectiveness of the following control technologies for the reduction of fugitive emissions:

- Double Mechanical Seals
- Rupture Disks
- Flares
- Valve Monitoring and Maintenance

2.7.2 Quantification of Fugitive Releases

Once the emission factors for the uncontrolled and controlled SOCMI fugitive emissions for each fugitive emission source are known, it is necessary to multiply each emission factor by the number of corresponding sources to quantify the fugitive releases per plant. The following data sources are useful in determining the number of fugitive emission sources in a SOCMI plant:

TABLE 8. UNCONTROLLED FUGITIVE EMISSION FACTORS FOR THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY (SOCMI)[1]

Fugitive-Emission Source	Uncontrolled Emission Factor (kg/hr)
Pumps	
Light liquids	
With packed seals	0.12
With single mechanical seals	0.12
With double mechanical seals	0.12[2]
With no seals	0.0
Heavy liquids	
With packed seals	0.020
With single mechanical seals	0.020
With double mechanical seals	0.020[2]
With no seals	0.0
Valves (in-line)	
Gas	0.027
Light liquid	0.011
Heavy liquid	0.0003
Safety-relief valves	
Gas	0.16
Light liquid	0.006
Heavy liquid	0.009
Open-ended valves	
Gas	0.025
Light liquid	0.014
Heavy liquid	0.003
Flanges	0.00056
Sampling connections	0.015
Compressors	0.64
Cooling towers	NA[3]
Agitators	NA[3]

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[1] These uncontrolled emission levels are based upon the refinery data presented in R. G. Wetherold, et al. February 1979. Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, p. 22, EPA Report No. 600/2-79-044; and subsequently modified in Wetherold, R. G., L. P. Provost and C. D. Smith. April 1980. Assessment of Atmospheric Emissions from Petroleum Refining, Vol. 3, Appendix 8, p. 266. EPA Report No. 600/2-80-075C.

[2] Assumes that the inner seal leaks at the same rate as single seal and that the VOC is emitted from the seal-oil degassing vent.

[3] No data available.

TABLE 9 . SELECTED FUGITIVE EMISSIONS CONTROL TECHNOLOGIES

Control Technology	Use	Effectiveness (% Emissions Removed)	Comments
Double mechanical seals[1]	Leakage reduction from rotary-type pumps and compressors	99%	Maximum service temperatures: <260°C
Rupture disks[1]	Prevent fugitive emissions through a relief-valve seat	100%	Requires a block-valve upstream to permit in-service replacement after disk rupture
Flare[1]	Closed loop sampling	99%	
Individual component survey[2]	Reducing valve emissions	30.7% (≤0.001)[3]	Directed maintenance involves simultaneous maintenance and screening of the valve until no further reduction could be recorded on a monitor
Unit area survey		48.7% (0.001-0.01)[3]	
Fixed point survey		93.8% (0.01-0.1)[3]	
Systems & directed maintenance		98% (>0.1)[3]	

[1] Source: Erikson, D. G. and V. Kalcevic, September 1980. Fugitive Emissions, prepared for USEPA/OAQPS/ESED.

[2] Source: Wetherold, R. G., L. P. Provost, and C. D. Smith, April 1980. Assessment of Atmospheric Emissions from Petroleum Refining: Volume 3, Appendix B.

[3] Source: Numbers in parenthesis refer to valve emissions from rate in lbs/hr.

1) Blacksmith, J.R., G. E. Harris and G. L. Langley, September 1980. Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units. EPA Report No. 600/2-81-003.
Provides useful screening data on the number and performance of items such as flanges, process drains, valves, pumps, and compressors for identified SOCMI processes.

2) White, R. E., 1980. Organic Chemical Manufacturing Volumes 6-10, Selected Processes. EPA Report No.s, EPA-450/3-80-028a-e.
Provides useful data on the number of equipment components for selected "model" processes.

3) In the absence of more detailed data, Erikson and Kalcevic (1980) follow the guidelines given below for estimating the number of equipment components and some of the characteristics for the process, assuming that the number of pumps is known.

Value to pump ratio = 25:1
Total number of sampling connections = 25% of the number of open-ended valves
Flange to valve ratio = 26:1
Pump seals, in-line valves = 50:50 split between light - and heavy-liquid service[2]

2.8 DATA RELIABILITY

The reliability of the environmental release data depends largely on the reliability of the data contained in the environmental release data base plus whatever data are provided in the PMN and by other sources. Since the ERDB will be used to estimate the environmental loadings for each "new" chemical, it is pertinent to discuss the reliability of the data contained therein.

Table 1-2(Appendix A) summarizes the information provided by each of the sources used to compile the ERDB. Data include the basis for reporting the emissions data, relation of emissions factors to plant size, form of reported emissions, data vintage, and data uncertainty (see also Section 2.2). The data uncertainty have four rankings (SAI 1981).

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[2] Heavy-liquid is defined as a fluid with vapor pressure equal to or less than 0.3 kPa at 20°C.

1. Emissions estimated from company site visits - data of reasonable accuracy.
2. Emissions estimated from data of indeterminate accuracy supplied by a company to state agencies.
3. Emissions estimated from data of indeterminate accuracy obtained from other published sources.
4. Emissions of indeterminate accuracy estimated without supporting data.

Most of the reports have a data uncertainty level of 3, indicating that most reports were at best secondary data sources, i.e., they reported data that were presented in other cited reports. Also of note are two further factors: 1) most of the reported emissions data draw on estimates rather than observed data, and 2) most of the reports use data that were generated more than five years ago.

In summary, the ERDB should be used cautiously in estimating environmental emissions from "new" SOCMI chemicals. Special care should be taken in using those tables that contain data from different plants of possibly different sizes and even from different eras. Since the SOCMI is dynamic in its response to new technological and legislative initiatives, current plant emission levels are lower than levels reported a few years ago. Thus more reliance may be put on recently completed studies (White, 1980).

2.9 AREAS FOR FURTHER RESEARCH

Table 10 lists the major limitations of the methodology and some of the assumptions on which it was based. Some of the suggested areas for further research flow naturally from the above table while others are more far-reaching. The research areas will be discussed under two headings: (1) expanding the environmental release data base and (2) broadening the applicability of the methodology.

TABLE 10. LIST OF LIMITATIONS OF THE METHODOLOGY

1. Environmental releases are estimated for steady-state, continuous processes of the SOCMI.

2. Releases due to accidents, spills, and process upsets are not estimated.

3. Releases resulting from (batch) cleaning operations are not accounted for.

4. No explicit procedure is provided for quantifying (unit process) solid wastes (including spent catalyst wastes).

5. Releases due to the provision of utilities are not estimated (e.g., furnace emissions, boiler blowdown, etc.)

6. In calculating storage, handling, and fugitive emissions, it is assumed that the SOCMI equipment emissions factors are equivalent to those prevailing in petroleum refinery operations.

7. The methodology tends to group the environmental releases under broad classes for air (VOC-volatile organic carbons) and water (BOD-biological oxygen demand, COD-chemical oxygen demand, TOC-total organic carbon).

8. The effects of feedstock variability on the generation of environmental residuals is not allowed for explicitly.

2.9.1 Expanding the Environmental Release Data Base (ERDB)

The ERDB can be expanded in quality (by conducting an expanded plant sampling program while simultaneously observing the kinds and numbers of plant operators working at each unit operation throughout the plant) and in breadth (by measuring the emissions associated with unit operations which heretofore had not been extensively observed, e.g., filtration processes).

Particular emphasis should be put on gathering data on batch manufacturing processes and on the amounts of spent catalyst sent for land disposal.

2.9.2 Broadening the Applicability of the Methodology

The methodology could be broadened to encompass the following possibilities:

(1) perform sensitivity analysis of the effects of variations in feedstock quality, process operating conditions and process upsets on the process environmental releases (in quality and quantity).

(2) generate reliable ranges of solid wastes produced for each unit process.

(3) estimate multimedia uncontrolled and controlled environmental releases on a compound-by-compound basis.

2.10 PRESENT DATA IN FORM REQUIRED FOR IN-PLANT AND EX-PLANT EXPOSURE ANALYSES

The format for presenting the data on environmental releases associated with the manufacture of a "new" chemical will be identical to the format used in presenting the environmental release data base (see Section 2.1 and Appendix A). Thus, the releases associated with the functioning of each plant unit operation are readily accessible and may be combined with information on the labor practices associated with the same unit operations to conduct an in-plant employee exposure analysis.

The execution of an off-plant exposure analysis (that incorporates a computer package such as ATM/SECPOP) to plant airborne emissions would take as its starting point the plant airborne emissions rate (broken down into the categories of emission type such as fugitive, process, and storage residuals) plus additional information on the physical and geographical characteristics of the emissions. These characteristics include (Hall, 1981):

- Geographic coordinates
- Source height (per emission type)
- Vent radius, vent gas temperature, ejection velocity (per emission type).

Valuable sources for making additional information on the characteristics of plant emission sources are:

1) SOCMI responses to emissions inventory questionnaires, particularly those prepared for the Texas Air Control Board and the Louisiana Air Board,
2) Reports on the manufacturing processes for 29 chemicals that were prepared by IT Enviroscience, Knoxville, TN, and appear as Appendices A-1 to A-29 in the report: Scientific Applications Incorporated, 1981. Human Exposure to Atmospheric Concentrations of Selected Chemicals (Draft Report), prepared for the Office of Air Quality Planning and Standards, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

Models and programs such as EXAMS and SESOIL that utilize in-plant vapor and solid waste emissions data in developing ex-plant pollutant concentrations are still under development by EPA/OTS and will not be discussed further.

3.0 EXAMPLE CALCULATION

Statement of the Problem: Estimate gaseous liquid and solid emissions resulting from the manufacture of ethylene dichloride, using the methodology outlined in Section 2. The only information supplied in the PMN is that required under Section 8 of TSCA (see Table 3.1). Compare the estimated environmental releases with results reported in the open literature (e.g., White (1980), Pervier (1974), Hedley (1975), and Chem Systems (1981).

3.1 UTILIZE THE ERDB

Consult Appendix A, Table A-12-8, for obtaining information on controlled and uncontrolled multimedia emissions from analogous processes. The information provided by this table will be utilized at appropriate points below in this example.

3.2 REVIEWING THE PMN

The only information supplied by the PMN is the required information under Section 8 of TSCA. Table 11 lists the information that would be provided on a PMN for ethylene dichloride. This is really not very much information, therefore the CEER report, ICR report, and ER report should be obtained from their respective branches of the EPA. Much engineering judgement will be employed.

A) Physical/chemical properties

Since this information is not available in the PMN, we would go to the Exposure Assessment Branch, USEPA and obtain the CEER report. See Section 3.3.1.

B) Product Impurities and Chemical Reactions Occurring

The following product impurities as specified in the PMN:

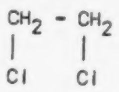
0.04% HCl
1.0% $CH_3CH_2Cl_2$

and traces of ethyl chloride and vinyl chloride

TABLE 11. MANUFACTURING INFORMATION CONTAINED IN THE PREMANUFACTURING NOTICE

A) Common or trade name: Ethylene Dichloride
Chemical identity: 1,2 Dichloro ethane

Chemical structure:



$\underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2}$

B) Production Volume - Capacity of 3,762,000 Mg/yr (1979)

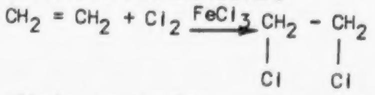
Total EDC production capacity	7,524,000 Mg/yr[1]	(1979)
50% by direct chlorination	3,762,000 Mg/yr[1]	
50% by oxychlorination	3,762,000 Mg/yr[1]	

We will pick a model plant size of 215,000 Mg/yr, operating 8760 hours a year, with 5-15% down time a year.[1]
Assume operating at 80% of capacity.

C) Proposed Categories of Use[1]

	Percent	Amount (1979)
Production of Vinyl Chloride	87	3,273,000
Production of 1,1,1 Trichloroethane	4	150,500
Production of Trichloroethylene	2	75,200
Production of Perchloroethylene	2	75,200
Production of Ethyleneamines	2	75,200
Production of Vinylidene Chloride	2	75,200
Used as a Lead Scavenger	1	37,600
	100	3,761,900

D) By-Products from Manufacture



$CH_2 = CH_2 + Cl_2 \xrightarrow{FeCl_3} \underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2}$

ethylene chlorine ethylene dichloride

Possible by-products are hydrogen chloride 0.04%[2]
ethylene trichloride 1.0%[2]
ethylchloride and vinyl chloride trace

E) Environmental and Health Effects

The ethylene dichloride vapor has an irritant effect on the respiratory tract and is toxic.[2]

F) Number of individuals exposed and their duration

2 8 hrs/day 5-10 ppm air

G) Method of Disposal

The chlorine and hydrogen chloride are absorbed in an aqueous absorber and treated in the wastewater treatment in the plant.[2]

The tars from the heavy end distillation column are landfilled.[2]

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[1] White 1980

[2] Pervier 1974

By obtaining the IRC report from the Industrial Chemistry Branch, USEPA, one can obtain more information about the reaction.

C) Process Information (Block Diagram, Mass Balances, and Location/Composition of Environmental Releases)

The block diagram, mass balance, and composition of environmental releases were not provided in the PMN. See Section 3.4 and 3.5 on how these items are dealt with.

D) Proposed Pollution Control Equipment/Disposal Practices

The proposed pollution control equipment and disposal practices have been outlined in the PMN. The reactor off-gas of HCl and excess chlorine will be treated by an aqueous absorber (scrubber) so that very little HCl or Cl_2 will be emitted to the atmosphere, but instead will be a water waste which will be treated in the waste treatment section of the plant. The PMN also says that the tars from the heavy ends distillation column will be landfilled.

E) Production Volume

For our example we will be considering a 215,000 Mg/yr plant operating 8760 hours a year with 5-15% downtime per year (White 1980).

3.3 CONDUCTING A CHEMISTRY REVIEW

3.3.1 Physical Chemistry Properties

The following information would be available (Perry 1973).

boiling point	82.4°C	
melting point	-35.3	
vapor pressure	@ 30°C	100 mmHg
molecular weight	98.96	
liquid at ambient conditions		
very slight soluble in water	0.43 g/100 mg (White 1980)	
specific gravity	1.2351^{20}	
log $K_{o/w}$ =	1.48 (Leo & Hansch 1979)	

3.3.2 Reaction Kinetics and Thermodynamics

We have already stated that the direct chlorination of ethylene to ethylene dichloride (EDC) will occur in the liquid phase over a ferric chloride catalyst. Since the boiling point of EDC is 82.4°C the reaction must occur at a temperature below this or at reduced pressures. Considine (1975) says that the addition of chlorine across a double bond can occur at a low temperature and a low pressure over a suitable catalyst ($FeCl_3$). Another factor pointing towards a low reactor temperature is that the reaction is exothermic releasing 218 kJ/mole of EDC (White 1980). Therefore, one would conclude that the reaction is occurring at low temperatures and reduced pressures. It is also known that the reaction is occurring at 38-49°C and 0.681-1.36 atm (69-138 kPa) (White 1980). Normally with a PMN this information would not be available.

The reaction is occurring in the liquid phase. Since gaseous reactants are being used the physical state in the reactor will be both liquid and gaseous. The reactor will have 2 exit streams: a liquid and a vapor stream. The product will be in the liquid stream and the reactor off-gases will exit from the reactor vent.

The reactants are fed in stoichiometric amounts; an excess of either reactant essentially results in raw material losses (Pervier 1974). A 90% yield is expected (Faith Clark and Keyes, 1965). If high-purity reactants are used then a 98% yield may occur. The impurities in the reactants are as follows:

Merchant chlorine contains:	(Pervier 1974)
chlorine	97.25%
oxygen	1.17%
carbon dioxide	0.54%
nitrogen	1.02%
hydrogen	0.03%
	100.01%

High-purity ethylene	(White 1980)
ethylene	99.9%
ethane	0.1%

A variety of catalysts may be used such as ferric, aluminum, or antimony chloride. In this case, a ferric chloride catalyst is chosen. Since it is a liquid phase reaction some of the catalyst will exit with the product. Therefore the catalytic bed is probably not regenerated. Fresh catalysts are added to the reactor to maintain the proper amount of catalysts. When the reactors are cleaned the catalysts are purged to a landfill and replenished.

3.4 CONDUCTING AN ENGINEERING ANALYSIS

Obtaining the Process Flow Diagram

Knowing that the direct chlorination of ethylene to ethylene dichloride is a halogenation reaction we will use the Halogenation Report (chapter 12, Appendix A). The process sequence of a halogenation is as follows: 1) halogenation, 2) absorption, and 3) separation. Using the generalized flow diagram in the halogenation report (Figure 3) and the information supplied in the PMN the process flow diagram in Figure 4 was constructed. The details that were added to the general halogenation diagram were various condensers, coolers, separators, pumps, reboilers, and the wastewater stripper. The wastewater stripper was added to strip any organics that may have been released to water during the scrubbing and washing operations. Engineering judgement was used in this case because it is common to have wastewater strippers in halogenation processes.

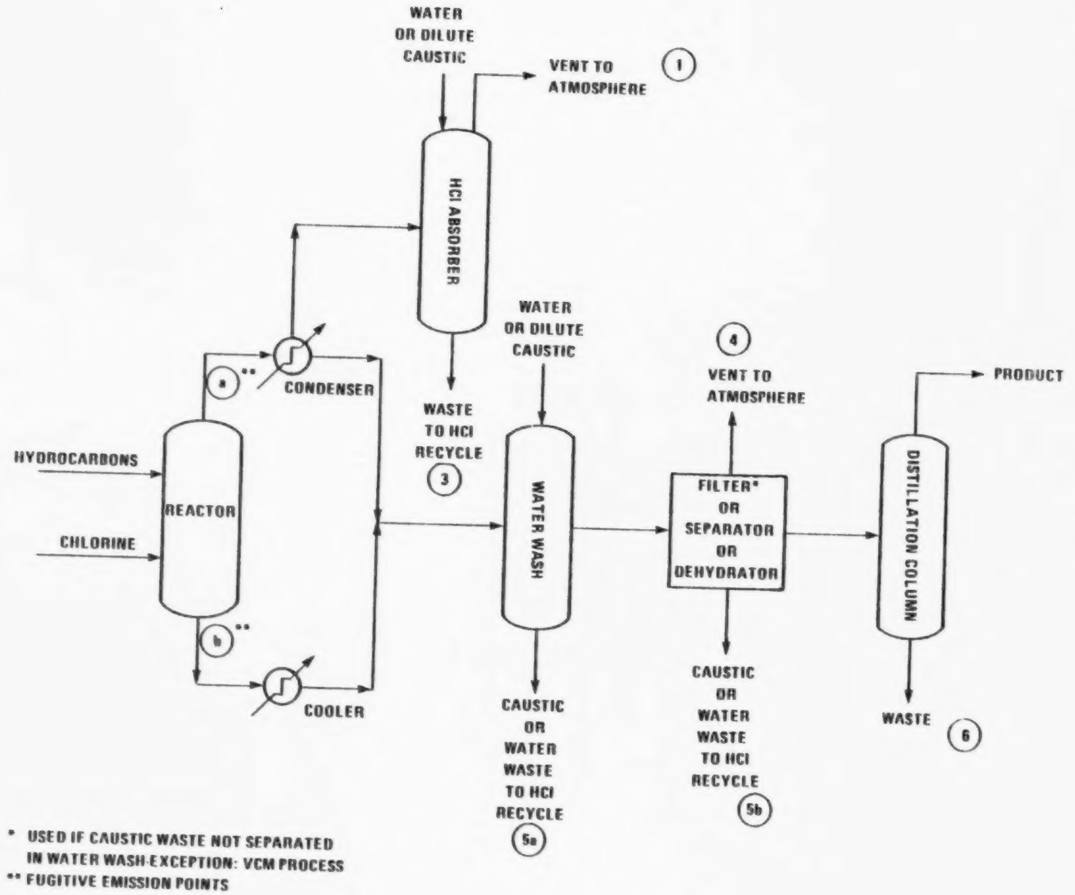
3.5 PROCESS RELEASES

3.5.1 Qualitative Analysis of Releases

3.5.1.1 By Unit Process

a. Air Emissions

The unit process with the second largest air emissions is halogenation. A large amount of inert-carrier gas is involved in a



* USED IF CAUSTIC WASTE NOT SEPARATED
IN WATER WASH-EXCEPTION: VCM PROCESS
** FUGITIVE EMISSION POINTS

FIGURE 3 HALOGENATION OF HYDROCARBON
SOURCE: KAHN ET AL, 1979

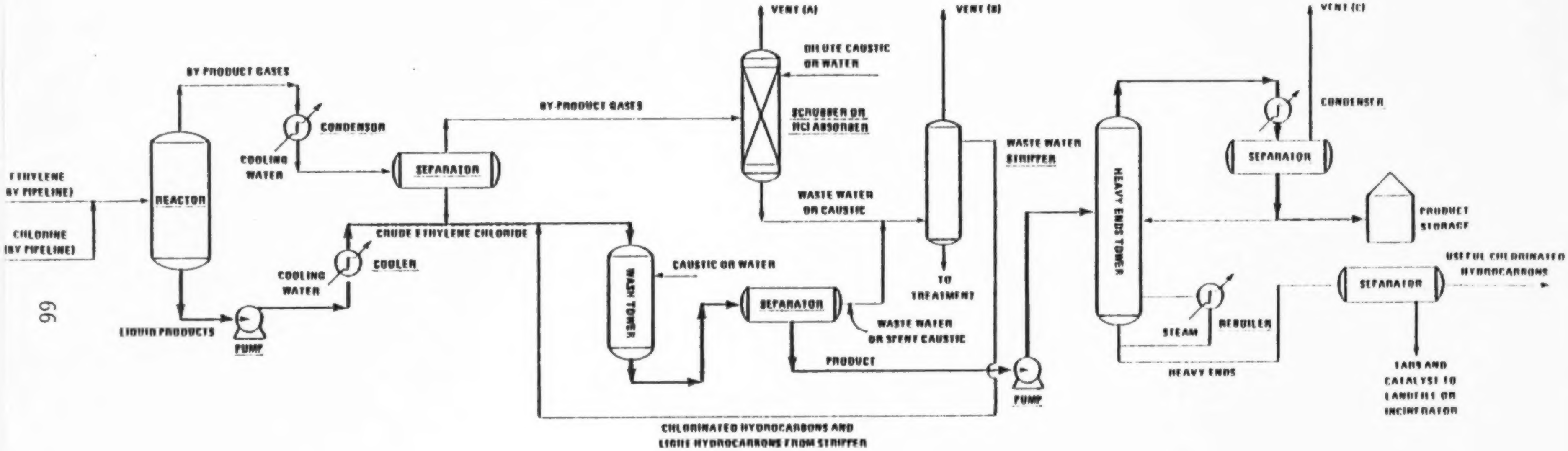


FIGURE 4 PROCESS FLOW DIAGRAM FOR MANUFACTURE OF ETHYLENE DICHLORIDE

halogenation reaction and removed by an absorber. Therefore, the direct chlorination of ethylene to ethylene dichloride will have large air emissions and the major source of air emissions will originate from the vent on the absorber.

b. Liquid Releases

The direct chlorination of ethylene to ethylene dichloride falls into subcategory B for water releases. Water is used as a vent gas absorbent and for the water wash of the liquid product. The spent water from both of these unit operations is sent to a wastewater stripper to remove organics. The wastewater will be largely contaminated with chlorine and HCl which will be removed in the HCl removal section of the wastewater treatment and recycled to the oxychlorination plant. Since water is only used as a scrubbing and washing medium and later treated for organics removal in the wastewater stripper, the liquid releases are assigned to Subcategory B's raw waste load with the following characteristics (from Table C-11):

Flow RWL	50-3,000	gal/1000 lbs
BOD_5 RWL	0.09-7.0	lb/1000 lbs
	50-500	mg/l
COD RWL	0.47-21.5	lb/1000 lbs
	200-5000	mb/l
TOC RWL	0.2-40	lb/1000 lbs
	100-2000	mg/l

Noncontact water is also used in the heat exchangers, condensers and reboilers. These raw waste loads can be used in ex-plant exposure analysis models.

C) Solid Wastes

The solid wastes from the direct chlorination of ethylene to ethylene dichloride will be the bottoms product of the heavy ends distillation column. This bottoms product consists of tars, useful chlorinated hydrocarbon and catalysts. The useful chlorinated hydrocarbons are separated out and sent to another process. The tars and catalysts will be landfilled.

3.5.1.2 Unit Operations

In this section, we will describe each piece of equipment and its associated environmental release.

Stoichiometric amounts of reactants enter the reactor. The reactor is a tubular reactor operating at 38-49°C and 0.68-1.36 atm (68-138 kPa). The heat released during reaction is 218 kJ/mole of product, therefore this heat is removed by jacketed walls, internal cooling coils or external heat exchange (Pervier 1974). A liquid and a vapor stream are obtained from the reactor. The vapor stream will consist of some ethylene dichloride, chlorine, hydrogen chloride, ethylene, and the inert-carrier gases. Most of the ethylene dichloride will exit in the liquid stream along with the other higher boiling components.

The vapor stream is sent to a condenser to condense any gaseous ethylene dichloride and other organics. These liquids are then separated from the gaseous by-products in a vapor-liquid separator and are combined with the liquid stream from the reactor and sent to the water wash. The uncondensed gases are sent to a HCl absorber or scrubber. Most of the hydrogen chloride and chlorine are separated out in the absorbing medium of water or dilute caustic. A less than 10% caustic solution should be used because greater concentration will enhance vinyl chloride formation from ethylene dichloride. The spent caustic or water is sent to the wastewater stripper to remove any dissolved organics. The wastewater is highly contaminated with HCl and Cl_2. Most of the organics and inert carrier-gases will exit to the atmosphere from the vent on the absorber.

The liquid stream from the reactor is sent to a cooler, combined with the liquids from the reactor condenser and passed to the wash tower. In the wash tower the liquid product is contacted with water or dilute caustic to remove any dissolved or entrained hydrogen chloride or chlorine. Since EDC is very slightly soluble in water they can be separated in a horizontal separator drawing EDC off the bottom and contaminated water off a sidearm. In some instances a drying column, a light ends column, or a filter are used instead of a horizontal separator. The crude EDC is pumped to a heavy ends tower to separate the product EDC from the heavy ends. The product EDC passes overhead and is sent to product storage. Any dissolved gases or uncondensed light ends are vented to the atmosphere from the condensing section on the column. The heavy ends consist of water, useful chlorinated hydrocarbons, tars, and catalysts. The useful chlorinated hydrocarbons are separated out in a horizontal separator and sent to further processing. The tars and catalysts are landfilled (White 1980, Pervier 1974, Kahn 1979, Faith, Clark and Keys 1965).

Table 12 is a summary of the possible sources of environmental release during the manufacturing of ethylene dichloride. This is a qualitative review of the releases resulting from the previous discussion.

3.5.2 Quantitative Analysis of Releases

3.5.2.1 Materials Balance

A materials balance has been made based on the assumption that stoichiometric amounts of the reactants will enter the reactor. For the production of 1000 kkg of EDC, the materials balance shown on Table 13 applies.

3.5.2.2. Quantification of Air Emissions

The inert-gas carrier method described by White (1980) is appropriate to be used. For determination of the air emissions released from the direct chlorination of ethylene to ethylene dichloride. We must first determine the molar ratio of total reaction-related carrier-gas flow to production rate, x given by Eq. (1).

TABLE 12. SUMMARY OF POSSIBLE SOURCES OF ENVIRONMENTAL RELEASE DURING THE MANUFACTURE OF ETHYLENE DICHLORIDE

Source	Releases	Receiving Medium
Leaks from reactor	-Organic or inorganic gases	Released to atmosphere
Leaks in cooling coils in jacketed reactor	-Water contaminated with organics	Released to air when water is processsed in cooling tower or will remain in water
Leaks in condensers, coolers, and reboilers	-Water contamination	Released to air when water is processed in cooling tower or will remain in water
Vent on absorber	-Largest source of air emissions	Released to atmosphere
Spent water or caustic from absorbers and wash tower and then wastewater stripper	-Water contaminated with organics & chlorides	Sent to stripper to remove organics: then sent to HCl remover to remove chlorides in wastewater treatment. Recovered chlorides are sent to oxychlorination reaction elsewhere in plant
Vent on wastewater stripper	-Vented gases organic & inorganic	Small stream released to atmosphere
Vent on condensation section of heavy ends tower	-Dissolved or entrained gases including light-ends	Released to atmosphere
Bottoms product of heavy ends tower	-Tars and catalysts	Landfilled

TABLE 13. MATERIALS BALANCE FOR ETHYLENE DICHLORIDE MANUFACTURE BY DIRECT CHLORINATION[1]

Basis: 1000 kg of ethylene dichloride production
Reactants are fed in stoichiometric amounts
90% conversion of reactants

Entering feed:

high purity ethylene	28.22 g/gmole	317 kkg
ethane	0.1% of ethylene	0.32 kkg
merchant chlorine	70.74 g/gmole	794 kkg
oxygen	1.17% of chlorine	9.6 kkg
carbon dioxide	0.54% of chlorine	4.4 kkg
nitrogen	1.02% of chlorine	8.3 kkg
hydrogen	0.03% of chlorine	0.25 kkg

Exiting stream:

ethylene dichloride	90% conversion 98.96 g/gmole	1000 kkg
ethylene trichloride	1.0% of product	11.1 kkg
hydrogen chloride	0.04% of product	0.44 kkg
chlorine	unreacted	79.4 kkg
ethylene	unreacted	31.7 kkg
ethane	inerts	0.32 kkg
oxygen	inerts	9.6 kkg
carbon dioxide	inerts	4.4 kkg
nitrogen	inerts	8.3 kkg
hydrogen	inerts	0.24 kkg
vinyl chloride	by-products	trace
ethyl chloride	by-products	trace
tars & catalysts	by-products	no avail. data
useful chlorinated hydrocarbons	by-products	no avail. data

---

[1] This materials balance is incomplete because of insufficient information on competing reactions.

$$G = C + H + R + P \tag{1}$$

$$C=[MCR \times (F_C-1) \times (1-S_C)] + MCR \times (1-P_C) \times F_C \times 2\ (1-S_{IN})]$$

$$H = MCHR \times (1-S_H)$$

$$H = MGRR \times F_{GR} \times (1-Y_{GR}) \times (1-S_{GR})$$

$$P = MGPR \times (1-S_G)$$

Separation efficiencies of the separation-recovery equipment are required for each gas to solve these equations. Efficiency ranges are supplied in White (1980) for the separation of the gases in an absorber.

$MCR = 1.0$	Molar ratio of chlorine to product = 1.0
$P_C = 93.2\%$	The molar purity of the chlorine = 93.2 mole % 97.25 wt %
$F_C = 1/0.9 = 1.111$	The molar ratio of the total chlorine feed to the stoichiometric requirement = 1. Include the unreacted chlorine from 90% yield = 1/0.9 = 1.111
$S_C = 0.95$	The separation efficiency of chlorine in the separation recovery equipment following the reaction. Assume the absorber is 95% efficient efficient (worst case)
$S_{IN} = 0.1$	The separation efficiency of the gaseous impurities in the chlorine in the separation equipment following the reaction. Separation of N_2, CO_2, H_2, and O_2 is not very efficient. In scrubbers - 10% efficient (worst case assumption)

Therefore, C, the molar ratio of chlorine-related gas flow to the production rate is:

$$C=[(1.0)(1.111-1)(1-0.95)] + [(1.0)(1-0.932)(1.111)(1-0.1)] = 0.0736$$

$MCHR = 0.04\%$	The molar ratio of hydrogen chloride to product = 0.04% from PMN
$S_H = 0.95$	The separation efficiency of hydrogen chloride in the separation-recovery equipment following the reaction. Assume the absorber is 95% efficient (worst case)

Therefore, H, the molar ratio of hydrogen chloride flow to the production rate is: $H = 0.0004\ (1-0.95) = 2 \times 10^{-5}$

$M_{GRR} = 1.0$ The molar ratio of gaseous organic reactant to product.

$F_{GR} = 1.0$ The molar ratio of total gaseous organic reaction to the stoichiometric requirement. Ethylene is added in strichiometric amounts.

$Y_{GR} = 0.9$ The molar overall reaction yield on the gaseous organic reactants. The yield was 90%.

$S_{GR} = 0.1$ The separation efficiency of the gaseous organic reactants in the separation-recovery equipment following the reaction. The absorber using water does not absorb organics very well, efficiency of 0.1 (worst case assumptions)

Therefore, R, the molar ratio of gaseous organic reactants flow to the production rate is: $R = (1.0)(1.0)(1-0.9)(1-0.1) = 0.09$

$M_{GPR} = 0.002$ The molar ratio of gaseous organic product to product manufactured. This was estimated, a small amount of ethylene dichloride will be in the gaseous state.

$S_{GP} = 0.1$ The separation efficiency of the gaseous organic products in the separation-recovery equipment. The absorber will not absorb ethylene dichloride very well (worst case assumption).

Therefore, P, the molar ratio of gaseous organic products to the production rate is: $P = (0.002)(1-0.1) = 0.0018$

And the resulting, G, the molar ratio of total reaction related carrier gas flow after the absorber is equip to:

$$G = 0.0736 + 2 \times 10^{-5} + 0.09 + 0.0018$$
$$G = 0.16542$$

$$G = 0.16542\left(\frac{\text{moles of gas}}{\text{mole of product}}\right) \times \frac{359\text{scf}}{1\ \text{lbmole of gas}} \times \frac{1\ \text{mole of EDC}}{98.96\ \text{lb}}$$

$$\frac{2.2046\ \text{lbs}}{\text{kg}} \times \frac{1000\ \text{kg}}{\text{kkg}} \times \frac{215{,}000\ \text{kkg}}{\text{yr}} \times \frac{1\ \text{yr}}{525{,}600\ \text{min.}} = 541.03\ \left(\frac{\text{scfm}}{215{,}000\ \text{kkg/yr}}\right)$$

Model plant capacity is 215,000 kkg/yr

The carrier-gas flow exiting the plant is 541.03 SCFM (standard cubic feet per minute) for this model plant.

Estimation of VOC

Ethylene is the major organic reactant comprising the emitted VOC and ethylene dichloride is the most volatile liquid organic.

Calculation of carrier-gas VOC in reactants and products

Pick the most volatile organic reactant - ethane
Pick the most volatile organic product - ethylene dichloride

R = 0.09 (moles of gaseous organic reactants/mole of product) MW = 28.22
P = 0.0018 (moles of gaseous organic products/mole of product) MW = 98.96

$$R\left(\frac{\text{scfm}}{\text{annual production}}\right) = 0.09\left(\frac{\text{moles of reactants}}{\text{mole of product}}\right) \times \frac{359\text{ scf}}{1\text{ lbmole of gas}} \times$$

$$\frac{2.2046\text{ lbs}}{1\text{ kg}} \times \frac{1000\text{ kg}}{\text{kkg}} \times \frac{215{,}000\text{ kkg}}{\text{yr}} \times \frac{1\text{ lbmole of product}}{98.96\text{ lbs}} \times \frac{1\text{ yr}}{525{,}600\text{ min}}$$

$$R = 294.4\left(\frac{\text{scfm}}{215{,}000\text{ kkg/yr}}\right)$$

$$R\left(\frac{\text{kkg}}{\text{yr}}\right) = 294.4\left(\frac{\text{scfm}}{215{,}000\text{ kkg/yr}}\right) \times \frac{1440\text{ min}}{\text{day}} \times \frac{365\text{ days}}{\text{yr}} \times \frac{1\text{ lbmole}}{359\text{ scf}}$$

$$\times \frac{28.22\text{ lbs}}{1\text{ lbmole}} \times \frac{1\text{ kg}}{2.2046} \times \frac{1\text{ kkg}}{1000\text{ kg}}$$

$$R = 5518.0\left(\frac{\text{kkg}}{\text{yr}}\right) \quad \text{for a } 215{,}000\ \frac{\text{kkg}}{\text{yr}} \text{ plant}$$

$$\frac{5517.9\text{ kkg/yr}}{215{,}000\text{ kkg/yr}} = 0.0256\ \frac{\text{kkg VOC}}{\text{kkg product}} = 25.67\ \frac{\text{kg VOC}}{\text{kkg product}}$$

Performing similar operations on the variable, P

$$P = 0.0018\ \frac{\text{moles of gaseous organic products}}{\text{mole of product}}$$

$$P = 5.889\ \frac{\text{scfm}}{215{,}000\text{ kkg/yr}}$$

P = 387.0 kkg/yr

P = 0.0018 kkg of VOC/kkg of product = 1.8 kg/kkg

Calculation of VOC from organic liquids or solids.

Assume the most volatile liquid or solid is ethylene dichloride. The calculation of VOC from EDC liquids is as follows: Vapor Pressure @21°C is 66 mmgHg.

$$Y_{VOC} = \frac{P_i^*(mmHg)}{760} = \frac{66}{760} \quad @\ 21°C$$

$$Y_{VOC} = 0.087$$

This is the worst case. We assumed the water vapor is saturated with ethylene dichloride and also that all VOC is the most volatile organic liquid.

$$VOC = \text{Organic liquid}\left(\frac{scfm}{\text{annual production}}\right) = G\left(\frac{Y_{VOC}}{1-Y_{VOC}}\right)$$

$$VOC = \left(541.03\ \frac{scfm}{215{,}000\ kkg/yr}\right)\left(\frac{0.087}{1-0.087}\right)$$

$$VOC = 51.55\ \left(\frac{scfm}{215{,}000\ kkg/yr}\right) \text{ of ethylene dichloride}$$

Vapors emitted from the model plant per year due to volatilization are

$$VOC\left(\frac{kkg}{yr}\right) = 51.55\ scfm \times \frac{1\ lbmole}{359\ scf} \times \frac{98.96}{1\ lbmole} \times \frac{525{,}600\ min.}{1\ yr} \times$$

$$\frac{kg}{2.2046\ lb} \times \frac{kkg}{1000\ kg} = 3388.11\ \frac{kkg}{yr}$$

$$VOC\left(\frac{kg}{kkg\ product}\right) = \frac{3388.11\ kkg/yr}{215{,}000\ kkg/yr} \times 1000 = \frac{15.76\ kg\ of\ VOC}{kkg\ of\ product}$$

The total estimated gas emitted from a 215,000 kkg of EDC/yr plant is:

I Total gas = total carrier-gas + total VOC evaporated from liquids

Total gas = G + VOC

$$\text{Total gas} = 541.03 + 51.55\ \frac{scfm}{yr} = 592.58\ \frac{scfm}{yr}$$

Total gas is chlorine and its impurities, VOC from the reactants and products, and VOC that evaporated from the organic liquids.

II Total VOC emitted = VOC in the carrier-gas (from reactants and products) + VOC evaporated from the liquids

$$\text{total VOC emitted} = 5518.0 + 387.0 + 3388.11 \ (\text{kkg/yr}) = 9293.11 \ \frac{\text{kkg of VOC}}{\text{yr}}$$

Total ratio of VOC emitted per kkg of EDC produced

$$\text{total ratio of VOC} = 25.67 + 1.8 + 15.76 \ \frac{\text{kg of VOC}}{\text{kkg EDC}} = 43.23 \ \frac{\text{kg of VOC}}{\text{kkg EDC}}$$

III Total inorganic gases emitted = Total carrier-gases (G) - VOC in Reactants (R) - VOC in products (P)

$$\text{Total } Cl_2, HCl, CO, H_2, CO_2, \text{ and } N_2 \text{ emitted} = 541.03 - 294.4 - 5.889 = 240.74 \ \frac{\text{scfm}}{215{,}000 \text{ kkg/yr}}$$

The previous calculation was evaluated by using the worst separation efficiencies of the separation-recovery equipment as estimated by White (1980). We have also calculated the emissions from EDC production using the best separation efficiencies of the separation-recovery equipment as estimated by White (1980). Table 14 shows the values of the variables used in these calculations for the maximum and minimum air emissions for comparison. The range of air emissions is 172-593 scfm for a 215,000 kkg/yr plant, with a resulting range of VOC emissions of 1640-9300 kkg of VOC/yr from the total plant. Most of this emission will exit through the absorber off-gas vent, a small portion with exit through the distillation column vents.

3.5.2.3 Quantification of Water Releases

Wastewater releases are estimated using raw water load at the unit process level plus information provided by the unit operation ranges

TABLE 14. MAXIMUM AND MINIMUM AIR EMISSION FROM EDC PRODUCTION BY EMISSION PROJECTION ESTIMATION

	Best Case	Worst Case
MCR	1	1
P_C	0.932	0.932
F_C	1.111	1.1111
S_C	0.999	0.95
S_{IN}	0.5	0.1
MCHR	0	0.0004
S_H	0.999	0.95
MGRR	1.0	1.0
F_{GR}	1.0	1.0
Y_{GR}	0.90	0.9
S_{GR}	0.9	0.1
MGPR	0.002	0.002
S_{GP}	0.9	0.1
C	0.0379	0.0736
H	0.0	2×10^{-5}
R	0.01	0.09
P	0.0002	0.0018
G	0.0481	0.1654
Total gas (G+VOC)	157.36 + 15.00 = 172.35	592.58 $\frac{\text{scfm}}{\text{yr}}$
Total VOC	613.11 + 43 + 985.45 = 1641.56	9293.11 $\frac{\text{kkg}}{\text{yr}}$
	2.85 + 0.2 + 4.58 = 7.634	43.23 $\frac{\text{kg of VOC}}{\text{kkg of EDC}}$
Total inorganics	157.36 - 32.715 - 0.654 = 124.	240.74 $\frac{\text{scfm}}{\text{yr}}$

of releases (Tables C-6 through C-8) and the materials balance. The wastewaters will eminate from the following three streams:

1) Absorber wastewater
2) Water wash wastewater
3) Wastewater stripper wastewater

The absorber and water wash wastewater, are sent to the wastewater stripper which strips out the organics, and recycles them to the water wash. The resulting wastewater will be highly contaminated with chlorides and a small amount of organics.

The quantified wastewater releases are detailed in Table 15.

3.5.2.4 Quantification of Solid Wastes

The solid wastes in the production of EDC will emanate from the heavy ends distillation as tars and catalysts. The range reported in Table C-7 is 1-100 kg of VOC/kkg of product. The total range estimated to be landfilled from a 215,000 kkg/yr plant is 215-21,500 kkg/yr. Chem Systems, Inc. reports a solid waste loss of 4600 kkg/yr for a 215,000 kkg/yr plant.

3.6 STORAGE AND HANDLING EMISSIONS

Ethylene and chlorine are piped in by pipeline (White 1980). We are mainly concerned with the storage and handling of ethylene dichloride. The liquid vapor pressure of EDC is 66 mmHg at 21°C (White 1980) or 0.086 atm (8.8 kPa). This vapor pressure falls in the range of both fixed-roof tanks and floating-roof tanks. White (1980) has conducted an industry survey and found that producers of EDC use fixed-roof tanks, half full and a 11°C diurnal temperature variation. White (1980) has also supplied the following data for 215,000 kkg/yr model-plant storage tanks:

No. of tanks required	1
Tank size	3800 m^3
Turnovers (per year)	12
Bulk temperature	27°C

TABLE 15. QUANTIFIED WASTEWATER RELEASES

Assumptions: Plant Production: 215,000 kkg/yr of EDC
Raw Water Load: 50-3000 gals/1000 lbs of EDC
Amount of Chlorine Entering the Absorber: 79.4 kkg/1000 kkg of EDC (See Table 13)
Separation Efficiency (%): 95-99 (See Table 14)
Ethylene Dichloride Concentration in the Wastewater is equal to the saturation concentration.

Physical Data: Solubility of Ethylene Dichloride in Water - 0.43 g/100 ml

Total Chlorides Discharged to the Wastewater:

$$\frac{215{,}000}{1{,}000} \times 78.6 \times (1-0.95) - \frac{215{,}000}{1{,}000} \times 78.6 \times (1-0.9) \text{ kkg/yr}$$

16,220 - 16,900 kkg/yr

Total Organics Exiting in the Wastewater Stream:

Using Subcategory B's estimated flow rates for

$$50\text{-}3{,}000 \text{ gal/1000 lbs} = 85.83 - 5149.7 \ \frac{\text{liters}}{\text{kkg}}$$

For a 215,000 kkg/yr plant the flow RWL rates are:

$$1.85 \times 10^7 - 1.107 \times 10^9 - \frac{\text{liters}}{\text{yr}}$$

Multiply by the solubility of ethylene dichloride to obtain a rough estimate of how much EDC is present in the exiting water stream:

$$79.4 - 4761 \ \frac{\text{kkg}}{\text{yr}} \text{ of EDC}$$

(0.04% - 2.2% of total production)

1) Breathing Emissions: using equation (1) in section 2.7

$$L_B = 9.15 \times 10^{-6} \times M \times \left[\left(\frac{P}{14.7-P}\right)^{0.68}\right] \times D^{1.73} \times H^{0.51} \times \Delta T^{0.5} \times F_p \times CK_c$$

L_B = Fixed roof breathing loss (kkg/yr)
M = 98.96 Molecular weight of vapor in storage tank (lb/lbmole)
P = 1.68 psia True vapor pressure at bulk liquid conditions
D = 55.5 ft Tank diameter
H = 27.75 ft Average vapor space height (use 1/2 tank height)
ΔT = 20°F Average diurnal temperature change (11°C)
F_p = 1.0 Paint factor (assume white tank in good condition)
C = 1.0 Adjustment factor for diameter tank
K_c = 1.0 Crude-oil factor

$$L_B = 9.15 \times 10^{-6} \times 98.96 \times \left[\left(\frac{1.68}{14.7-1.68}\right)^{0.68}\right] \times 55.5^{1.73} \times 27.75^{0.51} \times 20^{0.5} \times 1.0 \times 1.0 \times 1.0$$

To find D and H knowing the volume, we will assume that the diameter equals the height.

$$V = \pi r^2 h = 2\pi r^3 \qquad D = 16.9 \text{ m} = 55.5 \text{ ft}$$
$$h = 16.9 \text{ m} = 55.5 \text{ ft}$$

Resulting breathing loss is: 5.7 kkg/yr

2) The working losses from unloading and loading the storage tanks are found by equation 2 in Section 2.7.

$$L_W = 1.09 \times 10^{-8} M P K_n K_c V N$$

L_W = Fixed-roof working loss (kkg/yr)
N = 12 Turnovers per year
K_N = 1 Turnover factor
V = 1×10^6 gallons Tank volume (3800 m^3)

L_W = $1.09 \times 10^{-8} (98.96)(1.68)(1.0)(1.0)(1 \times 10^6)(12)$
L_W = 21.83 kkg/yr

The working losses are 21.83 kkg/yr.

Since the vapor pressure of the tars is so much lower than EDC, the storage losses will be negligible. The total emissions due to storage and handling are 27.53 kkg/yr.

3.7 FUGITIVE EMISSIONS

Fugitive emissions will occur from pumps, valves, compressor seals, flanges, and cooling towers. In order to quantify the fugitive emissions one must find the following information from literature.

1. Number of fugitive sources, for instance, how many pumps in plant
2. The kind of service supplied by these fugitive sources, such as, vapor-gas service or light-liquid service.
3. The appropriate uncontrolled and controlled released factors for each fugitive source.

The fugitive sources by their uncontrolled release factors. Table 16 shows our calculations for uncontrolled and controlled fugitive emissions from the model EDC plant. The number of fugitive sources were found in White (1980). We assumed that the fugitive sources were equal for an oxychlorination process and a direct-chlorination process because we had the numbers for a balanced process. The total uncontrolled fugitive emissions is 191.1 kkg of VOC/yr for a 215,000 kkg/yr EDC plant operating 8760 hours a year. If controls are placed on the seals of these pieces of equipment then the estimated release will decrease to 99.2 kkg of VOC/yr.

TABLE 16. CALCULATIONS OF FUGITIVE EMISSIONS

Pieces of Equipment	Uncontrolled Emission Factor kg/hr	Emission kg/hr	Controlled Emission Factor kg/hr	Emission kg/hr
21 pumps handling VOC				
19 handle EDC and other light liquid service	0.12	2.28	0.03	0.57
2 provide heavy-liquid	0.02	0.04	0.02	0.04
550 process valves				
100 gas/vapor service	0.027	2.7	0.002	0.02
450 light-liquid service	0.011	4.95	0.003	1.35
20 pressure relief valves in gas/vapor service	0.16	3.2	0.061	1.22
14,300 flanges, using a 26:1 flange to valve ratio	0.00056	8.01	0.00056	8.01
1 compressor seal	0.64	0.64	0.11	0.11
1 cooling tower	NA		NA	
Total fugitive emission kg/hr		21.82		11.32
Total fugitive emissions kkg/yr		191.1		99.2

4.0 CONCLUSIONS AND RECOMMENDATIONS

The viability of the methodology for estimating environmental releases associated with the manufacture of a "new" chemical has been demonstrated in the chosen example of the manufacture of ethylene dichloride (EDC) by the direct chlorination process. Methodological limitations and assumptions have been outlined in Table 10 . Areas for further endeavors in improving the methodology have been outlined in Section 2.9.

REFERENCES

Aynsley, Eric, and Meryl R. Jackson. 1971. Industrial Waste Studies: Steam Generating Plants. Prepared for USEPA - Water Quality Office, Washington, D.C.

Bucon, H. W., and J. Macko. 1978. Volatile Organic Compound (VOC) Species Data Manual. Prepared for USEPA, Research Triangle Park, North Carolina.

Blacksmith, J. R., G. E. Harris and G. L. Langley. January 1981. Frequency of Leak Occurrence for Fittings in Synthetic Organic Chemical Plant Process Units. USEPA/ORD, Washington, D.C. EPA-600/2-81-003.

Carpenter, B. H. 1974. Vinyl Chloride - An Assessment of Emissions Control Techniques and Costs. U.S. EPA. RTP, North Carolina: EPA-650/2-74-097.

Chem Systems Inc., New York, N.Y. July 7, 1981. Communication with Robert F. Golden, Putnam, Hayes, and Bartlett Inc., Cambridge, Massachusetts.

Considine, D. 1974. Chemical and Process Technology Encyclopedia, New York, New York: McGraw-Hill Book Company.

Erickson, D. G. September 1980. Storage and Handling. Report 1 of Organic Chemical Manufacturing, Volume 3: Storage, Fugitive and Secondary Sources. USEPA/OAQPS/ESED. RTP, North Carolina. EPA-450/3-80-025.

Erickson, D. G., and V. Kalceic. September 1980. Fugitive Emissions Report 2 of Organic Chemical Manufacturing, Volume 3: Storage, Fugitive, and Secondary Sources, USEPA/OAQPS/ESED. Research Triangle Park, North Carolina. EPA-450/3-80-025.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals, 3rd Ed. New York, New York: John Wiley and Sons, Inc.

Gruber, G. I., TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. U.S. Environmental Protection Agency. Office of Solid Waste. Washington, D.C. EPA/530/SW-118C.

Hall, Loren. October 1981. Presentation on the EPA/OPTS/OTS/CFB ATM-SECPOP Program.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publilshing Co., Inc.

Herrick, E. C., J. A., King, and R. P. Oullette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

REFERENCES (continued)

JRB Associates. 1980. Level II Materials Balance - Benzene. For: Office of Pesticides and Toxic Substances, Survey and Analysis Division. Washington, D.C.: U.S. Environmental Protection Agency. Draft Report.

Khan, Z. S., and T. W. Hughes. Monsanto Research Corporation. 1979. Source Assessment: Chlorinated Hydrocarbons Manufacture. U.S. Environmental Protection Agency. Industrial Environmental Research Laboratory. Research Triangle Park, North Carolina. EPA-600/2-79-019G.

Leo, A. and C. Hansch. 1979. Substituent Constants for Correlation Analysis in Chemistry and Biology. New York, New York: John Wiley and Sons.

Lyman, W., W. F. Reehl, and D. H. Rosenblatt (Eds.). 1982. Handbook of Chemical Property Estimation Methods, New York, New KYork: McGraw-Hill Book Company.

Perry, Robert H., and Cecil H. Chilton. 1973. Chemical Engineer's Handbook (5th Edition), New York, New York: McGraw-Hill Book Company.

Pervier, J. W. et al. April 1974. Survey Reports on Atmospheric Emissions from the Petrochemicals Industry (2 Volumes), USEPA/OAQPS, Research Triangle Park, North Carolina. EPA-450/3-73-005a&b.

Public Law 94-469. October 11, 1976. Toxic Substances Control Act.

Radian Corp. 1977. Industrial Process Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Research Triangle Park, North Carolina: Industrial Environmental Research Lab., U.S. EPA.

SAI. 1981. Human Exposure to Atmospheric Concentrations of Selected Chemicals (2 Volumes). Prepared for USEPA/OAQPS, Research Triangle Park, North Carolina.

U.S. EPA. Office of Solid Waste, November 14, 1980. Background Document. Resource Conservation and Recovery Act, Subtitle C - Identification and Listing of Hazardous Waste. Listing of Hazardous Waste (Finalization of May 19, 1980 Hazardous Waste List).

U.S. EPA. 1981. Supplement 12 for Compilation of Air Pollutant Emission Factor. Research Triangle Park, North Carolina: U.S. EPA, Office of Air and Water Management and Office of Air Quality Planning and Standards.

U.S. EPA. 1974a. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemical Manufacturing. Point Source Category. Washington, D.C.

U.S. EPA. 1974b. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Synthetic Resin Segment of the Plastics and Synthetic Materials Manufacturing Point Source Category. Washington, D.C.: U.S. EPA.

REFERENCES (continued)

Versar Inc. 1979. Production and Use of Benzene. Office of Water Planning and Standards. Washington, D.C.: U.S. Environmental Protection Agency.

Wetherold, R. G. and L. P. Provost. February 1979. Emission Factors and Fequency of Leak Occurrence for Fittings in Refinery Process Units. USEPA/ORD, Washington, DC. EPA-600/2-79-044.

Wetherold, R. G., L. P. Provost and C. D. Smith. April 1980. Assessment of Atmospheric Emissions from Petroleum Refining: (Volume 3, Appendix B Detailed Data Compilation), USEPA/ORD, Washington, D.C. EPA-600/2-80-075C.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volumes 6-10. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028a-e.

APPENDICES

APPENDIX A

THE ENVIRONMENTAL RELEASE DATA BASE (ERDB)

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1.0 INTRODUCTION

For the Synthetic Organic Chemicals Industry (SOCMI), it is convenient to organize an environmental release data base (ERDB) in terms of the 23 major large-volume SOCMI "unit process" components that carry out the fundamental synthesis reaction, e.g., alkylation, halogenation, etc. Conceptually, the unit process is useful in that for a given unit process, the physical or organic chemistry of the compounds within that unit process tends to be alike or similar. The significance of the process waste streams and the industrial importance of the compounds produced were also considered in the selection of the major unit processes (Herrick 1979).

This report describes how the environmental release data base (ERDB) is organized (Section 1.1) and then deals with its limitations (Section 1.2). The following 23 chapters give a comprehensive picture of the environmental releases for each of the 23 major identified unit processes.

1.1 Organization of the Environmental Release Reports

As mentioned previously, this report deals with the environmental releases of the 23 major SOCMI "unit processes." The 23 major unit processes are listed on page 89. The format that has been followed in preparing each of the 23 environmental release reports is shown in Appendix B.

Of particular importance in each chapter is the Summary of Emissions Data which is a compilation of the available release data for the large-volume SOCMI chemicals manufactured by the named unit process. Controlled and uncontrolled release data are presented for the three classes (process, storage and handling, and fugitive) in terms of the receiving medium (air, land, water). Process releases are further classified in terms of the unit operations that occasion the emissions.

It bears noting that storage and handling emissions occur during the storage and handling of plant items such as feedstock, intermediates, final products, usable by-products, waste tars, residues, non-usable by-products plus their tankage on site. Process releases are caused by the manufacturing process itself and can be related (both qualitatively and quantitatively) to each major unit operation in the manufacturing process train. Fugitive emissions are defined as those emissions that result from leaking plant equipment components such as pump-seals, in-line (process and control) valves, relief valves, open-ended (sample, drain, vent) valves, compressor seals, flanges, and cooling towers.

Table 2-2 is an example of how emissions data are reported and consists of 11 columns. The significance of each column is explained below:

Product:	Indicates the SOCMI chemical under review.
Pollutant:	Indicates the pollutant under study.
Location:	Indicates where in the process train the pollutant will be found.
Source:	Indicates whether the pollutant is contained in a reactant, product, by-product, solvent or waste stream.
Type of Releases:	Indicates whether a release is routine (r) or accidental (a).
Receiving Medium:	Air, land or water.

The next three columns refer to uncontrolled emissions.

Quantity:	The amount of pollutant generated (in kg) per kkg product.
Rate:	The generation rate of the pollutant (kg/hr).
Form:	Gas, liquid or solid.

The last two columns refer to controlled emissions.

Control Technology:	The control technology that is used in reducing the emission levels.
Quantity:	The amount of pollutants (in kg/kkg product) exiting from the environmental control system.

An additional feature of the table is that a citation is provided for every qualitative/quantitative item of data reported.

The Environmental Release Data Base (ERDB) consists of the set of available release data for the 23 cited unit processes. A listing of all the chemical products that make up the ERDB is given in Table 1-1. For each medium, the data source is identified plus an indication of whether quantified or unquantified data are available. Unfortunately, for reasons of respecting confidential business information (CBI), comprehensive information from the following sources was unavailable:

TABLE 1-1. CHARACTERIZATION OF THE ENVIRONMENTAL RELEASE DATA BASE BY UNIT PROCESS, CHEMICAL PRODUCT, RECEIVING MEDIUM, AND DATA SOURCE[2]

Unit Process	Chemical Product	Receiving Medium					
		Air		Water		Land	
		Qualitative	Numerical	Qualitative	Numerical	Qualitative	Numerical
Alkylation	Cumene	White	X	Wise			
	Ethylbenzene	White	X	Hedley	X		
				Wise			
	Linear alkyl benzenes	White	X				
	Lead alkyls			Gruber	X	Gruber	X
	Acetic acid	Wise		Wise			
Amination by Ammonolysis	Ethanolamines	White	X	White	X	Gruber	X
		Wilkins	X	Wilkins	X	White	X
						Wilkins	X
	Hexamethylenetetramine	Wilkins	X	Wilkins	X		
	Choline chloride	Wilkins	Receiving medium not available				
Ammoxidation	Acrylonitrile	White	X	Gruber	X	Gruber	X
				Wilkins	X	Wilkins	X
	Benzonitrile	Wilkins	X				
	Hydrogen cyanide	Pervier	X				
Carbonylation	Acetic acid	Hedley	X			Hedley	X
		White	X				
	Ethyl acrylate	Hedley	X	Hedley	X	Hedley	X
	n-Butyraldehyde	Hedley		Hedley			
	n-Butanol	Hedley					
	2-Ethylhexanol	Hedley	X			Hedley	
Condensation	Acetic anhydride	White	X				
		Hedley		Hedley			
	Bisphenol A			Hedley	X		
	Crotonaldehyde	Hedley		Hedley			
	Ethyl ether			Hedley			
	2-Ethyl hexanol	Hedley	X				
	Hexamethylene tetramine	Hedley		Hedley			
	Methyl isobutyl ketone			Hedley			
	Methyl parathion	Gruber	X	Gruber	X		
	Pentaerthyritol	Hedley		Hedley		Hedley	
	Polyethylene terephthalate					Hedley	X
	Pyridine			Gruber	X	Gruber	X
Catalytic cracking	Isoprene			Hedley	X		
	Vinyl chloride	Hedley	X			Gruber	X

(continued)

TABLE 1-1. CHARACTERIZATION OF THE ENVIRONMENTAL RELEASE DATA BASE BY UNIT PROCESS, CHEMICAL PRODUCT, RECEIVING MEDIUM, AND DATA SOURCE (Continued)

Unit Process	Chemical Product	Receiving Medium					
		Air		Water		Land	
		Qualitative	Numerical	Qualitative	Numerical	Qualitative	Numerical
Dehydrogenation	Styrene	SAI	X	Hedley	X	Hedley	X
				Wise			
	Isoprene	Hedley	X	Hedley	X		
	Butadiene			Hedley	X		
	Methyl ethyl ketone			Hedley			
	Butadiene (n-butane)	White	X				
	Butadiene (n-butene)	White	X				
	Linear alkyl benzenes	White	X				
Dehydrohalogenation	Polycarbonate resins	Hedley		Hedley	X		
	Vinyl chloride	Hedley	X	Wise		Hedley	X
	Vinylidene chloride	White	X	Hedley	X		
Esterification	Dimethyl terephthalate			Wise			
		Wilkins	X	Wilkins	X		
		White	X	Hedley	X		
	Ethyl acrylate	Hedley	X	Hedley	X		
	Methyl methacrylate	Hedley	X	Hedley	X	Hedley	X
	Polyethylene terephthalate			Hedley	X	Hedley	X
	Isopropyl acetate			Wilkins	X		
	Ethyl acetate			Wilkins	X		
	Diisodecyl phthalate			Wilkins	X		
	Diethyl phthalate	Wilkins		Wilkins	X		
	n-Butyl acetate	Wilkins	X	Wilkins	X		
Halogenation	Chlorobenzene	Gruber	X	Gruber	X	Gruber	X
		Khan	X				
		White	X				
	Vinyl chloride monomer	Gruber	X	Gruber	X	Gruber	X
	Allyl chloride	Hedley	X				
	Chloroprene	Hedley		Hedley	X		
	Trichloroethylene	Hedley	X				
	Perchloroethylene	Gruber	X	Gruber	X	Gruber	X
	Ethyl dichloride	Hedley	X	Hedley	X	Hedley	X
		White	X	Khan	X		
		Khan	X				
	Chloromethanes	Gruber	X	Gruber	X		
		White	X	White	X		
	Chlorotoluene					Gruber	X

TABLE 1-1. CHARACTERIZATION OF THE ENVIRONMENTAL RELEASE DATA BASE BY UNIT PROCESS, CHEMICAL PRODUCT, RECEIVING MEDIUM, AND DATA SOURCE (Continued)

Unit Process	Chemical Product	Receiving Medium					
		Air		Water		Land	
		Qualitative	Numerical	Qualitative	Numerical	Qualitative	Numerical
Hydrodealkylation	Benzene	Versar	X	Versar	X	Versar	
		JRB		Wise			
Hydrogenation	Adiponitrile	Hedley	X	Hedley	X	Hedley	X
	Aniline	White	X	White			
	Cyclohexane	White	X				
	Cyclohexanol	White	X				
	Hexamethylenediamine			Hedley	X	Hedley	X
				Wise			
Hydrohalogenation	1,1,1-Trichloroethane	White	X	Hedley	X		
		Hedley	X				
	Vinyl chloride	Hedley	X				
		Carpenter	X				
	Glycerin	White	X	Hedley	X	Hedley	X
		Hedley	X				
	Choline chloride	Wilkins	Receiving medium not available				
Hydrolysis	Ethylene glycol	White	X	Hedley	X		
	Methyl ethyl ketone			Hedley			
	Isopropyl alcohol	Hedley		Hedley	X		
	Sec-butyl alcohol			Hedley			
	Ethyl alcohol	Hedley	X	Hedley	X		
	Propylene oxide	Wilkins	X				
		SAI	X				
	Chlorobenzene			Wilkins	X	Wilkins	X
Nitration	Nitrobenzene	Hedley	X	Gruber	X	Gruber	
		White	X	Faith	X		
	Toluene diisocyanate (TDI)	White	X				
Oxidation	Acetaldehyde			USEPA 1980	X		
	Acetic acid	White	X	Hedley	X		
		Hedley	X				
	Acrolein	Hedley	X				
	Acrylic acid & esters	White	X				
	Adipic acid - cyclohexane	AP-42	X				
	Adipic acid - cyclohexanol	White	X				
	Cyclohexanone/anol	White	X	Hedley	X		

TABLE 1-1. CHARACTERIZATION OF THE ENVIRONMENTAL RELEASE DATA BASE BY UNIT PROCESS, CHEMICAL PRODUCT, RECEIVING MEDIUM, AND DATA SOURCE (Continued)

Unit Process	Chemical Product	Receiving Medium					
		Air		Water		Land	
		Qualitative	Numerical	Qualitative	Numerical	Qualitative	Numerical
Oxidation (continued)	Ethylene oxide	Hedley	X	Wise	X		
	Ethylene glycol	Hedley	X				
	Formaldehyde methanol	AP-42	X	AP-42	X		
	Glycerine	White	X				
	Isophthalic acid			Hedley			
	Maleic acid	AP-42	X				
		White	X				
	Phenol/acetone	White	X	USEPA 1980	X		
	Phthalic anhydride	AP-42	X	USEPA 1980	X		
	Terephthalic acid	AP-42	X	Hedley	X		
Oxyhalogenation	Ethylene dichloride	Khan	X	Khan		Khan	
		TRC	X				
		White	X				
		Hedley	X			Hedley	X
	Trichloroethylene and Perchloroethylene	Khan	X	Khan		Khan	
		White	X				
Phosgenation	Toluene diisocyanate (TDI)			Wise			
		White	X	Hedley	X	Hedley	X
	Diphenylmethane-4-4'-diisocyanate (MDI)					Hedley	X.
	Polycarbonate resins			Hedley	X		
Polymerization	Unsaturated polyester			Hedley	X		
	Polycarbonate resins	Hedley		Hedley	X		
	Epoxy resins	Hedley				Hedley	X
	Polypropylene	Hedley	X				
	Polystyrene-butadiene resin (SBR)	Hedley		Hedley			
	Styrene-acrylonitile (SAN)	Hedley					
	Acrylonitrile-butadiene-styrene (ABS)			Hedley	X		
	Polystyrene	Hedley	X	Hedley	X		
	Polyethylene	Hedley	X	Hedley	X		
	Polyvinyl chloride (PVC)	Hedley	X	Hedley	X		
	Polyvinyl acetate	Hedley	X	Hedley	X		

TABLE 1-1. CHARACTERIZATION OF THE ENVIRONMENTAL RELEASE DATA BASE BY UNIT PROCESS, CHEMICAL PRODUCT, RECEIVING MEDIUM, AND DATA SOURCE (Continued)

Unit Process	Chemical Product	Receiving Medium					
		Air		Water		Land	
		Qualitative	Numerical	Qualitative	Numerical	Qualitative	Numerical
Polymerization (continued)	Polyvinyl alcohol			Hedley	X		
	Amino resins			Hedley	X		
	Nylon 6			Hedley	X	Hedley	X
	Nylon 66	Hedley	X	Hedley	X	Hedley	X
	Polychloroprene	Hedley		Hedley			
	Polyethylene terephthalate			Hedley	X	Hedley	X
	Polyacrylonitrile	Hedley		Hedley			
	Polyisoprene	Hedley	X	Hedley	X		
	Polybutadiene	Hedley	X	Hedley	X		
	Ethylene polyethylene resins	Hedley	X	Hedley	X		
Pyrolysis	Ethylene	Radian	X	Radian		Radian	X
		White	X				
Reforming/water-gas	Methanol	White	X	USEPA 1974a	X		
				Hedley	X		
Sulfonation	Methyl methacrylate	White	X	Gruber	X		

---

[1] For each of the media (air, water, land), the data are characterized as qualitative or numerical.

1) Pertinent publications under PEP '81 and earlier phases of the Process Economics Program which is managed by SRI International, Menlo Park, California.

2) Data base for Review of BATEA Effluent Limitations Guidelines, NSPS, and Pretreatment Standards for the Organic Chemicals Industry, prepared under the aegis of the Organic Chemicals Branch of the Effluent Guidelines Division of the EPA.

1.2 Limitations of the Environmental Release Data Base

The reliability of the environmental release data depends largely on the character of the data sources that were cited in its formulation. Table 1-2 summarizes the information provided by each of the sources used to compile the ERDB. Data include the basis for reporting the emissions data, relation of emissions factors to plant size, form of reported emissions, data vintage, and data uncertainty. The data uncertainty has four rankings (SAI, 1981).

1. Emissions estimated from company site visits - data of reasonable accuracy.
2. Emissions estimated from data of indeterminate accuracy supplied by a company to state agencies.
3. Emissions estimated from data of indeterminate accuracy obtained from other published sources.
4. Emissions of indeterminate accuracy estimated without supporting data.

Other limitations of the ERDB refer more to the applicability of the data provided i.e., release data are reported for steady state operations and tend to be classified under broad classes (such as volatile organic carbons for air). Table 10 lists applicability limitations of the method.

Table 1-2. Evaluation of the Quality of Information Provided by Various ERDB Sources

		Basis for Reporting Emissions Data				Form of Reported Emissions					
Data Source	Year Pub.	Plant Samp.	Materials Balance	Estimates	Emissions Data Explicitly Show Effects of Plant Scale	Gas	Liquid	Solid	Data Vintage	Data Uncertainty	Comments
Bucon & Macko	1978	×		×	No	×			1972-1978	2-3	Data include species material prepared for the California Air Control Board
Carpenter	1974			×	Yes	×			<1974	3	
Faith Keyes & Clark (3rd Ed.)	1965			×	No		×		1963	4	No explanation is provided on how emissions were calculated: No bibliography is provided
Formica	1976	×		×	No	×			<1974	3-4	Data compiled for 8 SOCMI processes
Gruber	1975		×	×	No	×	×	×	up to 1973	3	Data utilized were taken primarily from prior EPA reports plus "best estimates of experienced industry personnel"
Hedley	1975			×	No	×	×	×	1967 onwards	3	Most data were transcribed from old SRI Process Economic Program Reports
JRB	1980		×	×	No	×	×	×	up to 1979	3	

Table 1-2. Evaluation of the Quality of Information Provided by Various ERDB Sources
(Continued)

Data Source	Year Pub.	Basis for Reporting Emissions Data: Plant Samp.	Materials Balance	Estimates	Emissions Data Explicitly Show Effects of Plant Scale	Form of Reported Emissions: Gas	Liquid	Solid	Data Vintage	Data Uncertainty	Comments
Khan & Hughes	1979	x		x	Yes	x			1976-1977	1-2	Data are based on plant sampling plus some engineering estimates
Pervier	1974			x	No	x			Pre 1974		Results from an Industry survey are reported
Putnam, Hayes & Bartlett	Aug. 1981	x		x	No	x	x	x	1977-1980	1-3	Reports qualitative data on the chlorinated organics Industry
Radian	1977			x	Yes	x	x	x	1970-1976	3	
SAI	1981	x		x	No	x			1978	1-4	These data were compiled by IT Enviroscience under subcontract to SAI
USEPA	1974	x	x	x	Yes		x		1973-1974	1	
USEPA	1980			x			x		1968-1978	3	Data sources Include other EPA reports and SRI/PEP reports
USEPA (AP-42)	1981			x	Yes	x				3	
USEPA, OAQPS	Aug. 1981	x		x	No	x			1976-1978	2-4	Efficacy of control technology equipment for oxidation processes Is reported

Table 1-2. Evaluation of the Quality of Information Provided by Various ERDB Sources
(Continued)

		Basis for Reporting Emissions Data				Form of Reported Emissions					
Data Source	Year Pub.	Plant Samp.	Materials Balance	Estimates	Emissions Data Explicitly Show Effects of Plant Scale	Gas	Liquid	Solid	Data Vintage	Data Uncertainty	Comments
USEPA Treatability Manual	Sept. 1981	×			No		×		1977-	1	Limited quantitative data from the EPA/EGD/OCB SOCMI verification program reported
Versar	1979		×	×	No	×	×	×	1977-1978	3	
White Vols. 6-10	1980	×	×	×	Yes	×	×	×	1974-1979	1-2	Data mainly collected from emissions inventory questionnaires (EIQ) and from other published sources
Wilkins et al.	1980			×	No	×	×	×	<1976	2-3	Limited emissions data are reported, including data that were compiled by Monsanto under an earlier contract (Pre 1976)
Wise/Fanrenthold	1981			×	No		×		1977-	1	Reports qualitatively the results of EPA/EGD/OCB SOCMI verification program

---

[1] Emissions data have four levels of uncertainty (Hydroscience Inc., Knoxville, Tennessee quoted in p. 206 of SAI (1981)).

1. Emissions estimated from company site visit - data of reasonable accuracy.
2. Emissions estimated from data of indeterminate accuracy supplied by a company to state agencies.
3. Emissions estimated from data of indeterminate accuracy obtained from other published sources.
4. Emissions of indeterminate accuracy estimated without supporting data.

1.3 REFERENCES

Bucon, H.W., and J. Macko. 1978. Volatile Organic Compound (VOC) Species Data Manual. Prepared for USEPA, Research Triangle Park, North Carolina.

Carpenter, B. H. 1974. Vinyl Chloride - An Assessment of Emissions Control Techniques and Costs. U.S. EPA. Prepared for RTP, North Carolina: EPA-650/2-74-097.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals, 3rd Ed. New York, New York: John Wiley and Sons, Inc.

Formica, Peter N. September 1976. Controlled and Uncontrolled Emission Rates and Applicable Limitations for Eighty Processes. Prepared for EPA/OAQPS/Control Program Development Division, Research Triangle Park, NC Under Contract #68-02-1382, Task Order #12.

Gruber, G. I., TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. U.S. Environmental Protection Agency. Office of Solid Waste. Washington, D.C.: EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. 1975. Potential Pollutants from Petrochemical Proceses. Westport, Connecticut: Technomic Publishing Co., Inc.

Herrick, E. C., J. A., King, and R. P. Oullette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

JRB Associates. 1980. Level II Materials Balance - Benzene. For: Office of Pesticides and Toxic Substances, Survey and Analysis Division. Washington, D.C.: U.S. Environmental Protection Agency. Draft Report.

Khan, Z. S., and T. W. Hughes. Monsanto Research Corporation. 1979. Source Assessment: Chlorinated Hydrocarbons Manufacture. For Environmental Protection Agency. Industrial Environmental Research Laboratory. Research Triangle Park, North Carolina. EPA-600/2-79-019G.

Pervier, J.W. et al. April 1974. Survey Reports on Atmospheric Emissions from the Petrochemicals Industry (2 Volumes), USEPA/OAQPS, Research Triangle Park, North Carolina. EPA-450/3-73-004A&B.

Putnam, Hayes & Bartlett, Inc. August 1981. An Industry Approach for the Regulation of Toxic Pollutants. Prepared for USEPA Toxics Integration Project.

REFERENCES (continued)

Radian Corp. 1977. Industrial Process Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Research Triangle Park, North Carolina: Industrial Environmental Research Lab, U.S. EPA.

SAI. 1981. Human Exposure to Atmospheric Concentrations of Selected Chemicals (2 Volumes). Prepared for USEPA/OAQPS, Research Triangle Park, North Carolina.

U.S. EPA. Office of Solid Waste, November 14, 1980. Background Document. Resource Conservation and Recovery Act, Subtitle C - Identification and Listing of Hazardous Waste. Listing of Hazardous Waste (Finalization of May 19, 1980 Hazardous Waste List).

U.S. EPA. August 1981. Air Oxidation Processes in the Synthetic Organic Chemicals Manufacturing Industry - Preliminary Draft EIS. U.S. EPA/OAQPS - Emission Standards and Engineering Division, Research Triangle Park, NC.

U.S. EPA. 1981. Supplement 12 for Compilation of Air Pollutant Emission Factor. Research Triangle Park, North Carolina: U.S. EPA, Office of Air and Water Management and Office of Air Quality Planning and Standards.

U.S. EPA. Sept. 1981. Treatability Manual Volume II. Industrial Descriptions. Prepared for U.S. EPA, Office of Research and Development, Washington, D.C. 20460. EPA Publication No. EPA-600-8-80-042b.

U.S. EPA. 1974a. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemical Manufacturing. Point Source Category. Washington, D.C.

Versar Inc. 1979. Production and Use of Benzene. For: Office of Water Planning and Standards. Washington, D.C.: U.S. Environmental Protection Agency.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volumes 6-10. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-023.

Wilkins, G.E., C. H. Tucker and E.D. Gibson. September 1980. The Revised Organic Chemical Producers Data Base (OCPDB) System. Prepared for U.S. EPA, Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268. EPA Publication No. EPA-600/PS2-80-164.

SECTION 2 - ALKYLATION

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SECTION 2

ALKYLATION

2.0 INTRODUCTION

Alkylation is the introduction of an alkyl radical into an organic compound by substitution or addition (Herrick et al. 1979a). The process is a catalytic reaction employing an acidic alkylation catalyst such as solid phosphoric acid, aluminum chloride, sulfuric acid, hydrogen fluoride, or aluminum chloride.

After reaction, the effluent is usually separated from the catalyst mixture in a settler. The alkylated hydrocarbon is sent to separation and purification, which involves a series of columns. The first in the series is a feedstock hydrocarbon stripper in which the excess unreacted organic feed is distilled off as overhead. The bottoms of this column are separated in subsequent columns into product and useful by-products. If the acid is not removed between reaction and separation steps, vent gas from the reactor and separation columns is scrubbed of acid (from the catalyst) via a caustic scrubber (White 1980). Figure 2-1 illustrates a general alkylation process.

Alkyl-metallic manufacture is different from other alkylation processes in that it is not catalytic. A typical process is lead alkyls manufacture (Figure 2-2). A 90:10 weight ratio of lead to sodium alloy is prepared in an alloy pot, cooled, and sent to an autoclave reactor. Ethyl chloride is introduced into this reactor, and alkylation takes place at 5.1 to 5.2 atm and 65 to 70°C. Waste hydrocarbons that are produced are discharged to the atmosphere. The effluent is fed to a still where product tetraethyl lead (TEL) is stripped from the lead and sodium chloride using water as a wash. TEL and water vapor are condensed and sent to a decanter where TEL is drawn off as bottoms. TEL is then washed, settled, and blended with ethylene dichloride, ethylene, dibromide, and dyes for final product (Gruber 1975).

The most common alkylation products are ethylbenzene and cumene. Other products and their 1980 production are found in Table 2-1.

FIGURE 2-1. GENERALIZED PROCESS FLOW DIAGRAM FOR MANUFACTURE OF ALKYLATED ORGANIC COMPOUNDS. SOURCE: WHITE, 1980; KIRK-OTHMER, 1978.

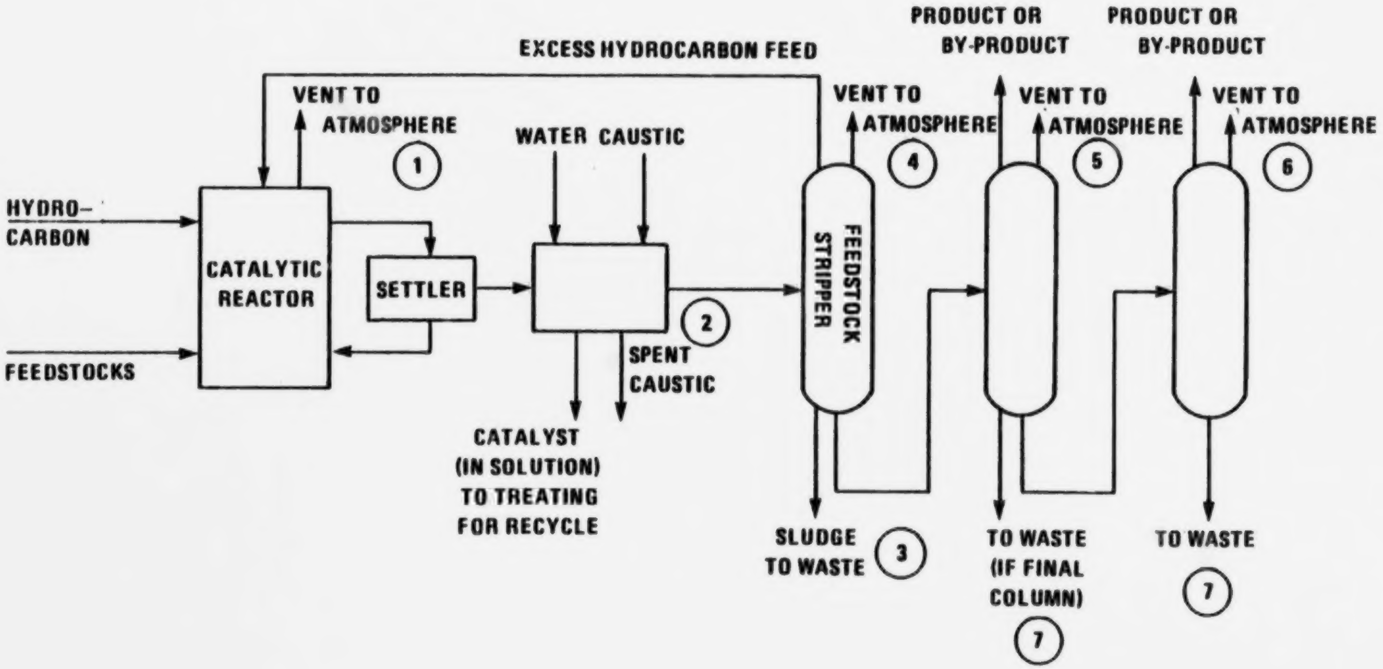
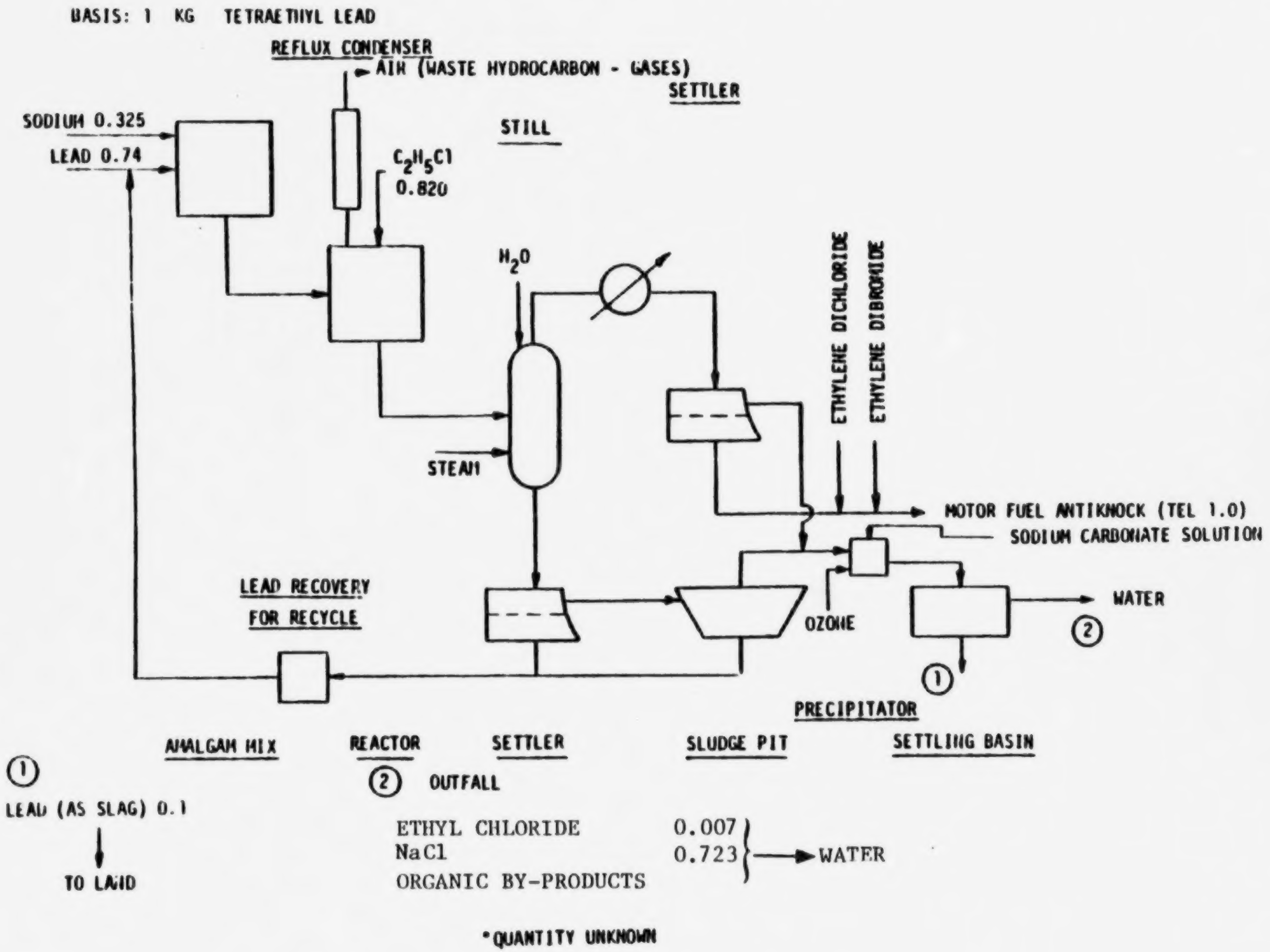


FIGURE 2-2. LEAD ALKYLS MANUFACTURE



Source: Gruber 1975.

TABLE 2-1. ALKYLATION PRODUCTS AND THEIR MANUFACTURE IN 1980

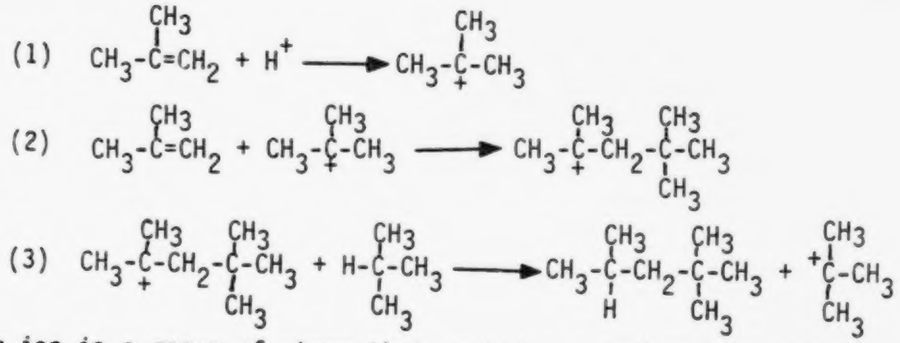
Product	Amount* kkg	Feedstock	Other Required Processes
Acetic acid	NA	n-Butenes	Oxidation
Alkylbenzenes	94,347	Benzene Propylene tetramer	None
Alkylbenzenes (linear)	87,090	Benzene Linear olefins	None
Alkylbenzenes (linear)	157,850	Benzene Linear paraffins	Dehydrogenation
Benzene, xylenes	NA	Toluene	None
p-tert-Butylphenol	NA	Phenol Isobutene	None
Cumene	1,932,304	Benzene Propylene	None
Ethylbenzene	3,516,611	Benzene Ethylene	None
N-Isopropyl-N'-phenol-p-phenylenediamine	NA	p-Chloronitrobenzene Aniline Acetone	Dehydrohalogenation Hydrogenation
Lead alkyls	>259,455	Ethyl chloride (Alkyl chlorides)	None
p-nonyl phenol	147,690	Phenol Propylene trimer	None
Phenol, acetone	1,436,255	Benzene Propylene	Acid cleavage Hydrolysis Oxidation
Pyromellitic deanhydride	NA	1,2,4-trimethylbenzene (pseudocumene)	Oxidation
Styrene	3,263,688	Benzene Ethylene	Dehydrogenation
2,4-xylenol	NA	p-cresol Methylchloride	None

*SRI lists amounts in plant capacities. For this table, the capacities were multiplied by 0.8.

Source: Herrick et al. 1979a; SRI 1981

2.1 GENERAL CHEMISTRY

During alkylation, a carbonium ion reaction takes place in the following three steps:



(1) $CH_3-\overset{CH_3}{C}=CH_2 + H^+ \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_3$

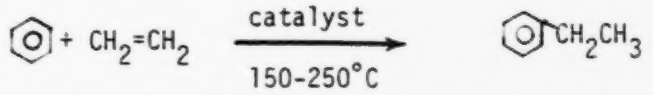
(2) $CH_3-\overset{CH_3}{C}=CH_2 + CH_3-\underset{+}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

(3) $CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + H-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + {}^{+}\underset{CH_3}{\overset{CH_3}{C}}-CH_3$

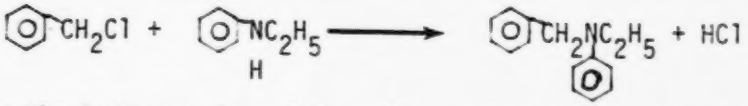
A carbonium ion is a group of atoms that contains a carbon atom bearing only six electrons instead of the usual eight. In step (3), the carbonium ion abstracts a hydrogen atom (hydride ion) from a molecule of alkane. The resulting new carbonium ion can continue the chain (Morrison and Boyd 1973).

Of the five basic types of alkylation reactions, three involve substitution for hydrogen: 1) on nitrogen, 2) on carbon, and 3) in a hydroxyl (Herrick et al. 1979a). The other two types are alkyl-metallic formation and the formation of quaternary ammonium compounds. Equations for those five reactions are below:

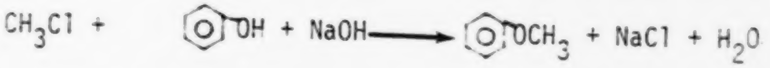
a. The most common alkylation reaction is the substitution for hydrogen on a carbon:



b. Secondary and tertiary amines are formed with the substitution for hydrogen on a nitrogen:



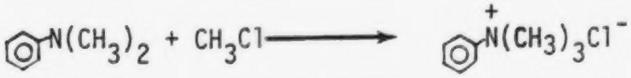
c. When the hydrogen in a hydroxyl is substituted, the result is an ether:



d. Alkyl-metallic formation involves a carbon-to-metal bond:

$$4C_2H_5Cl + 4PbNa \longrightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

e. The following is an example of quaternary ammonium compound formation:



Other radicals besides organics and metals can add or substitute on an organic compound:

$$CH_2{=}CH_2 + SiHCl_3 \xrightarrow{\text{catalyst}} C_2H_5SiCl_3$$

$$n\text{-}C_{12}H_{25}Cl + NaSH \longrightarrow nC_{12}H_{25}SH + HCl$$

2.2 DESCRIPTION OF DISCHARGE

Releases from the alkylation processes occur as fugitive and particulate gaseous emissions, liquid wastes, and solid residues. The major sources of air contamination are: 1) feedstock emissions and 2) volatile by-products.

Wastewaters may be released from within the process if process operating conditions require. They may also occur from washdown of process vessels, or they may be formed during chemical reactions. These waste streams contain caustic and caustic-catalyst fines, and feedstock lead (from the lead alkyls process) will result from distillation column bottoms and product settling basins.

fugitive gaseous emissions	- may occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains, and cooling towers.
reactor	- gaseous releases may occur at the reactor vent.
caustic scrubber	- liquid waste may occur from caustic wash.
feedstock stripper	- gaseous releases may occur from the column vent. - sludge may be released as wastewater from the column bottoms.
purification columns	- gaseous releases may occur from the column vent. - liquid wastes may be released in the column bottoms.

2.3 DESCRIPTION OF AN EXAMPLE PRODUCTION PROCESS: CUMENE MANUFACTURE

The manufacture of cumene by the addition of propylene to benzene consists of four major steps: 1) catalytic reaction, 2) depropanization, 3) benzene recovery, and 4) cumene distillation. Figure 2-3 illustrates this process. For each part, the description highlights the emissions associated with that step of the process.

2.3.1 Catalytic Reaction

Propylene-containing propane and excess benzene are fed to a reactor containing an acidic catalyst, solid phosphoric acid on a support such as alumina. The reaction is carried out in the vapor phase at high temperature of 205°C and a pressure of 34.5 atm. The effluent exits the bottom of the reactor and is sent to purification (White 1980).

2.3.1.1 Emissions

The reactor bottoms contain solid waste catalyst. The waste stream contains volatile organic chemicals. Fugitive emissions may occur at process pumps, piping flanges, and valves (White 1980).

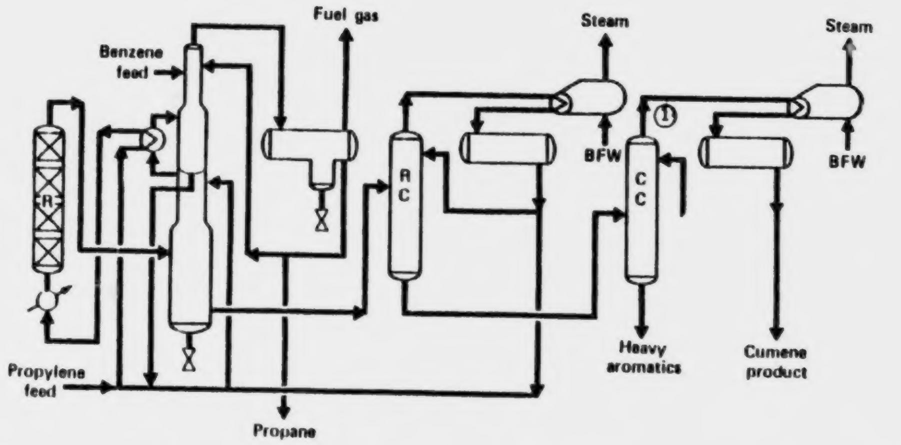
2.3.2 Depropanizer Column

The unreacted propane that was present in the propylene feed is drawn off as overhead gas in the depropanizer column. The system is blanketed with methane or nitrogen to avoid the contact of air with cumene. This "blanket" of methane or nitrogen gas surrounds the column and is encased in a jacket. Bottoms contain cumene and are sent to further purification (White 1980).

2.3.2.1 Emissions

Vent to the fuel gas system contains methane, propane, and inert gases. The contaminated waste stream contains dissolved volatile organic chemicals, mainly benzene. Fugitive emissions may occur at process pumps, piping flanges, and valves (White 1980).

FIGURE 2-3. CUMENE MANUFACTURING PROCESS



UOP catalytic condensation process for cumene synthesis. R = reactor; RC = recycle column; CC = cumene column; BFW = boiler feed water.

Source: Kirk-Othmer, Vol. 7, 1980.

2.3.3 Benzene Recovery

This column is operated under pressure, and the system is again blanketed with methane or nitrogen. Benzene exits the column as overhead and cumene in the bottoms goes to further purification (White 1980).

2.3.3.1 Emissions

The vent to the fuel gas system bleeds off methane (or nitrogen), benzene vapor, and inert gases. The purge stream, which goes to recycle, contains ethylbenzene and similar low boilers (White 1980).

2.3.4 Cumene Distillation

This is the final purification step for cumene. The column is operated at slightly above atmospheric pressure and blanketed with methane or nitrogen to avoid the contact of air with cumene. Overhead gas contains cumene and methane, and it goes through a condenser. Pure cumene is condensed and sent to storage (White 1980).

2.3.4.1 Emissions

The purge vent on the condenser bleeds off methane and cumene vapor. The waste stream contains mostly diisopropylbenzene and small amounts of other high-boiling materials. It is returned to the refinery for use in the gasoline pool or as fuel (White 1980).

2.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the following manufacturing processes:

- Cumene (Table 2-2)
- Ethylbenzene (Table 2-3)
- Linear alkylbenzenes (LAB) (Table 2-4)
- Lead alkyls (Table 2-5)
- Acetic acid (Table 2-6)

The locations of emissions sources for Tables 2-3 and 2-4 are found by consulting Figure 2-1; the location of those sources mentioned in Table 2-5

TABLE 2-2. CHARACTERIZATION OF EMISSIONS FROM THE CUMENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
	(Refer to Figure 2-3)								
C_2	Cumene column overhead (1)	feedstock	r	air	0.00351[1]	0.1053[1]	gas		
C_3	Cumene column overhead (1)	by-product	r	air	0.00117[1]	0.0351[1]	gas		
C_4	Cumene column overhead (1)	by-product	r	air	0.00183[1]	0.0549[1]	gas	plant flare	0.0015[2]
Benzene	Cumene column overhead (1)	feedstock	r	air	trace	NA	gas		
Alkylbenzenes	Cumene column overhead (1)	product and by-products	r	air	0.0235[1]	0.705[1]	gas		
Aromatics	Process effluents	by-products	r	water	NA[3]	NA	liquid	various	NA
Total VOC	Pump seals, valves, flanges	feedstocks, products, and by-products	a	air	0.24[1]	6.32[1]	gas	detection and corrections of major leaks	0.070[2]

---

†Indicates that release is routine (r) or accidental (a).

[1] White, Vol. 7, Section 3, p. IV-2. Based on annual production of 227,000 kkg/year.

[2] White, Vol. 7, Section 3, p. V-2.

[3] Wise and Fahrenthold, 1981. (See Table 3) Concentrations reported were greater than 0.5 ppm. Benzene is one of the feedstocks.

TABLE 2-3. CHARACTERIZATION OF EMISSIONS FROM THE ETHYLBENZENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
	(Refer to Figure 2-1)								
Benzene	Reactor vent (1)	feedstock	r	air	0.29[2]	10[2]	gas	process heater	0.00004[3]
	Column overhead vents (4,5)		r	air	1.7[2]	58[2]	gas	flare	0.017[3]
	Fugitive		a	air	0.11[2]	3.8[2]	gas	detection and correction of major leaks	0.029[3]
	Benzene recovery column bottoms (3)		r	water	11[1]	NA	liquid	NA	NA
Hydrogen chloride	Benzene column bottoms (3)	by-product	r	water	3.85[1]	NA	liquid	NA	NA
Aluminum salts	Product column bottoms (7)	catalyst fines	r	water	trace	NA	liquid (in solution)	NA	NA
	Dealkylation reactor (not shown)		r	water	7.05[1]	NA	liquid (in solution)	NA	NA
Aromatics . Polyaromatics Phenol	Process effluents	by-product	r	water	NA[4]	NA	liquid	NA	NA
Sodium hydroxide and sodium chloride	Product column bottoms (7)	additive and by-product	r	water	1.9[1]	NA	liquid (in solution)	NA	NA
Tarry matter	Dealkylation reactor (not shown)	by-product	r	water	21.55[1]	NA	liquid	NA	NA
Other VOC	Reactor vent (1)	by-product and feedstock	r	air	0.59[2]	20[2]	gas	process heater	0.00116[3]
	Column overhead (4) and (5)		r	air	0.9[2]	32[2]	gas	flare	0.009[3]
	Fugitive		a	air	0.4[2]	13.2[2]	gas	detection and correction of major leaks	0.111[3]

+Indicates that release is routine (r) or accidental (a).

[1] Hedley, p. 165. Based on 10,433 kkg/year.

[2] White, Vol. 6, Section 5, p. IV-4. Based on annual production of 300,000 kkg/year styrene production. Emissions may include styrene section.

[3] White, Vol. 6, Section 5, p. V-2.

[4] Wise and Farenthold, 1981. See Table 3. Concentrations reported were greater than 0.5 ppm. Benzene and Ethylene are the feedstocks.

TABLE 2-4. CHARACTERIZATION OF EMISSIONS FROM THE LAB MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Refer to Figure 2-1)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Benzene	Azeotrope column (not shown)	feedstock	r	air	0.0037[1]	0.038[1]	gas	used as fuel	(7.4×10^{-7})[2]
	HFl Scrubber(2)		r	air	0.011[1]	0.11[1]	gas	used as fuel or flare	(2.2×10^{-6})[2]
Other VOC	Paraffin stripper(4)	by-products	r	air	0.088[1]	0.9[1]	gas	surface	(7.0×10^{-3})[2]
	By-product stripper(5)	and feedstock	r	air	0.001[1]	0.01[1]	gas	none	0.001[1]
	Product column(6)		r	air	0.0000014[1]	0.000014[1]	gas	none	0.0000014[2]

+ Indicates that release is routine (r) or accidental (a).

[1] White, Vol. 7, Section 7, p. IV-4. Based on annual production of 90,000 kkg/yr.
[2] White, Vol. 7, Section 7, p. V-3.

TABLE 2-5. CHARACTERIZATION OF EMISSIONS FROM THE LEAD ALKYLS MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Refer to Figure 2-2)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Lead (as slag)	Settling basin(1)	feedstock	r	land	100[1]	NA	solid	NA	NA
Ethylchloride	Settling basin overflow(2)	feedstock	r	water	7[1]	NA	liquid	NA	NA
Sodium chloride	Settling basin overflow(2)	by-product	r	water	723[1]	NA	liquid (in solution)	NA	NA
Organic by-products	Settling basin overflow(2)	by-product	r	water	NA	NA	liquid	NA	NA

+ Indicates that release is routine (r) or accidental (a).

[1] Gruber, 1975, p.5-48. Based on annual plant production of 18,000 to 100,000 kkg/yr.

TABLE 2-6. CHARACTERIZATION OF EMISSIONS FROM THE ACETIC ACID MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Refer to Figure 2-1)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Hydrocarbons	NA	by-product	r	NA	1.6	NA	NA	NA	NA
Carbon monoxide	NA	NA	NA	NA	2.2	NA	NA	NA	NA
Ethane	NA	NA	NA	NA	1.1	NA	NA	NA	NA
Methane	NA	NA	NA	NA	0.8	NA	NA	NA	NA
Butane	NA	feedstock	r	NA	4.2	NA	NA	NA	NA
Acetone	NA	NA	NA	NA	0.5	NA	NA	NA	NA
Acetaldehyde	NA	feedstock	NA	NA	0.5	NA	NA	NA	NA
Methyl acetate	NA	NA	NA	NA	0.5	NA	NA	NA	NA
Acetic acid	separator	product	NA	water	NA	NA	liquid	NA	NA
Alcohols	separator	NA	NA	water	NA	NA	liquid	NA	NA
Aldehydes	separator	NA	NA	water	NA	NA	liquid	NA	NA
Esters	separator	NA	NA	water	NA	NA	liquid	NA	NA
High boiling impurities	separator	feedstock	r	water	NA	NA	NA	NA	NA
Ketones	separator	NA	NA	water	NA	NA	NA	NA	NA
Propane	separator	NA	NA	air	NA	NA	gas	NA	NA

Source:

[1] EPA 1981. Organic Chemical Producers Data Base.

are found in Figure 2-2; and for Table 2-2, they are found in Figure 2-3. Releases are characterized as either routine (r) or accidental (a), controlled or uncontrolled. Catalytic waste amounts were not available for all the chemicals studied, and only air emissions were available for some of the chemicals.

REFERENCES

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. For Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitg et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemica Processes. Technomic Publishing Company, Inc. Westport, Connecticut.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979a. Unit Process Guide to Organic Chemicals Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Kirk-Othmer. 1971. Encyclopedia of Chemical Technology. 3rd Ed. Volume 7. New York: John Wiley and Sons.

Morrison, R. T., and R. N. Boyd. 1973. Organic Chemistry, 3rd Ed. Boston, Massachusetts: Allyn and Bacon, Inc.

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 6. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028a.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 7. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028b.

Wilkins, G. E., C. H. Tucker, and E. D. Gibson. September 1980. The Revised Organic Chemical Producers Data Base. Prepared for the Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

Wise, Hugh J. Jr. and Paul D. Fahrenthold. November 1981. Predicting Priority Pollutants from Petrochemical Processes. Environmental Science and Technology, 15, (11), pp. 1292-1304.

SECTION 3 - AMINATION BY AMMONOLYSIS

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SECTION 3

AMINATION BY AMMONOLYSIS

3.0 INTRODUCTION

The formation of amines by reacting ammonia with organic compounds is the process of amination by ammonolysis. Many products of amination, such as methylamines, ethylamines, ethanolamines, aniline, and ethylene diamines (see Table 3-1), result from a catalytic reaction, using a catalyst such as metallic silver, nickel, or copper or alumina, clay, or aluminum silicate. The reaction takes place in a vapor phase perfomed at moderately high temperatures and medium pressures. Following amination, the mixtures enter (1) a noncondensible gas separator, (2) an ammonia recovery column, (3) a dehydrator to draw off water, and (4) one or more distilling columns to obtain the desired products (Cocuzza et al. 1979; Habermann 1979; Klabunde 1979). A basic flow diagram and potential points of emission are shown in Figure 3-1.

Slightly different processes are used for the manufacture of the following products: (1) ethylenediamine from ethanolamine, which operates at a relatively high pressure of 250 atm.; (2) ethanolamines, produced in an aqueous liquid phase without a catalyst; and (3) ethylenediamine from ethylene dichloride in an aqueous liquid phase of a fractionating column (Figure 3-2) (Herrick et al. 1979b).

3.1 GENERAL CHEMISTRY

Amination can be described by the following equation:

$$RX + NH_3 \longrightarrow RNH_2 + HX$$

Two additional ammonolytic reactions involve the use of reactants other than ammonia: (1) aminolysis, in which primary and secondary amines act as aminating agents, and (2) hydroammonolysis, in which ammonia-hydrogen mixtures are used with a hydrogenation catalyst (such as supported metallic nickel, silver, or copper (Herrick 1979b). The following equations describe these reactions:

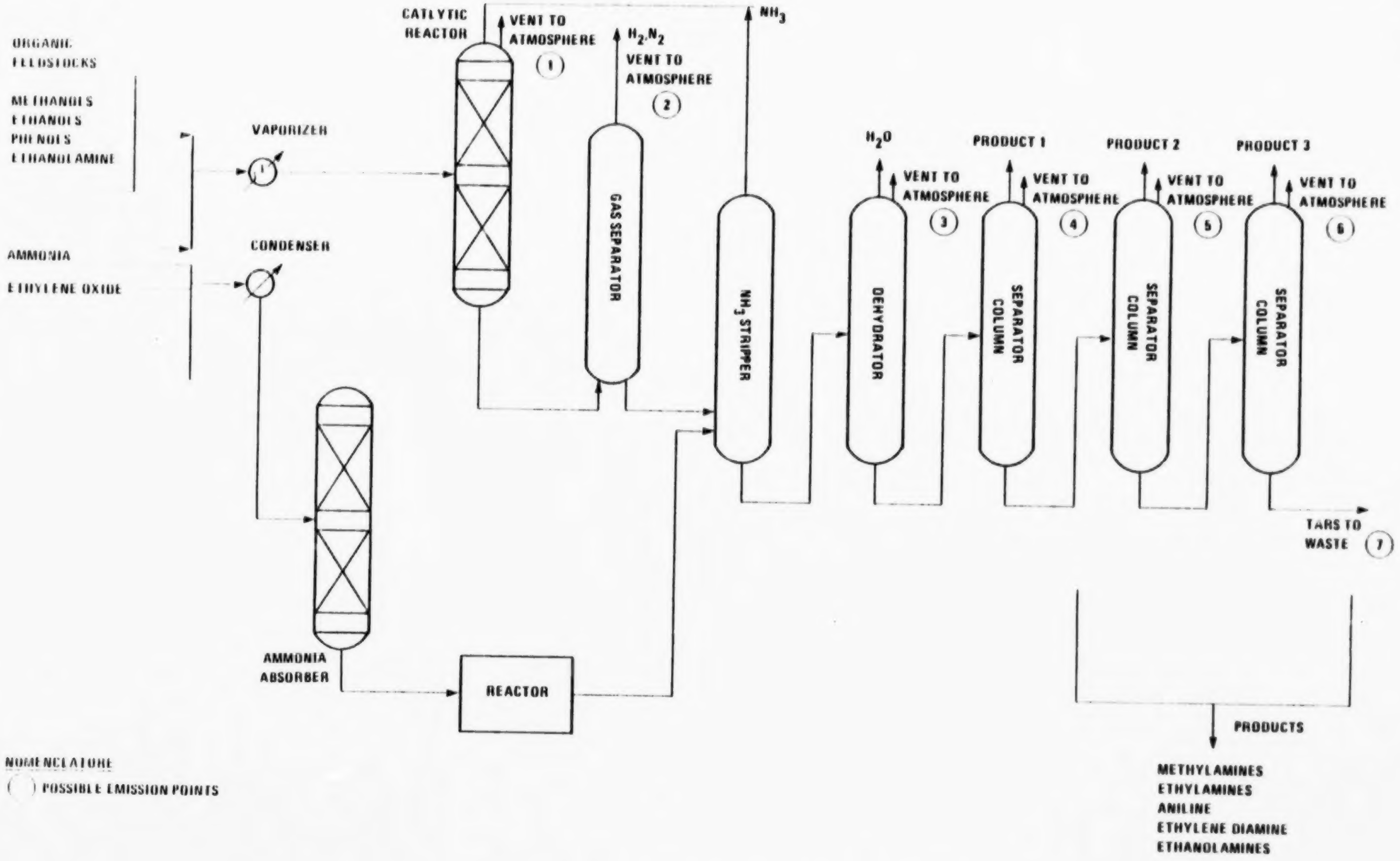


FIGURE 3-1. GENERALIZED FLOW DIAGRAM OF AMINATION PLANT (TWO OPTIONS: CATALYTIC AND NON-CATALYTIC REACTORS)
SOURCE: HERRICK, ET AL. 1979b.

TABLE 3-1. AMINATION PRODUCTS AND THEIR MANUFACTURE IN 1980.

Product	Amount kkg	Feedstock	Other Required Processes
Aniline	NA	Phenol	
Benzene sulfonamide	NA	Benzene sulfonyl chloride	
Choline Chloride	26,100	Ethylene oxide Trimethylamine	
p-Chlorobenzene sulfonamide	NA	p-Chlorobenzene Sulfonyl chloride	
Dimethyl-formamide	NA	Dimethylamine Methyl formate	
Ethanolamines	194,138	Ethylene oxide	
Ethanolamines	NA	Ethanol	
Ethylenediamine	72,575*	Ethylene dichloride	
Ethylenediamine	NA	Monoethanolamine	
Hexamethylenediamine	145,150	Adipic acid	
Hexamethylenetatramine	54,068	Formaldehyde	Condensation
Methylamines	134,989	Methanol	
Urea	2,580,759 (total)	Carbon dioxide	Dehydration

Source: Herrick, et al. 1979a; SRI 1981, USITC 1979.

*Feedstock not specified

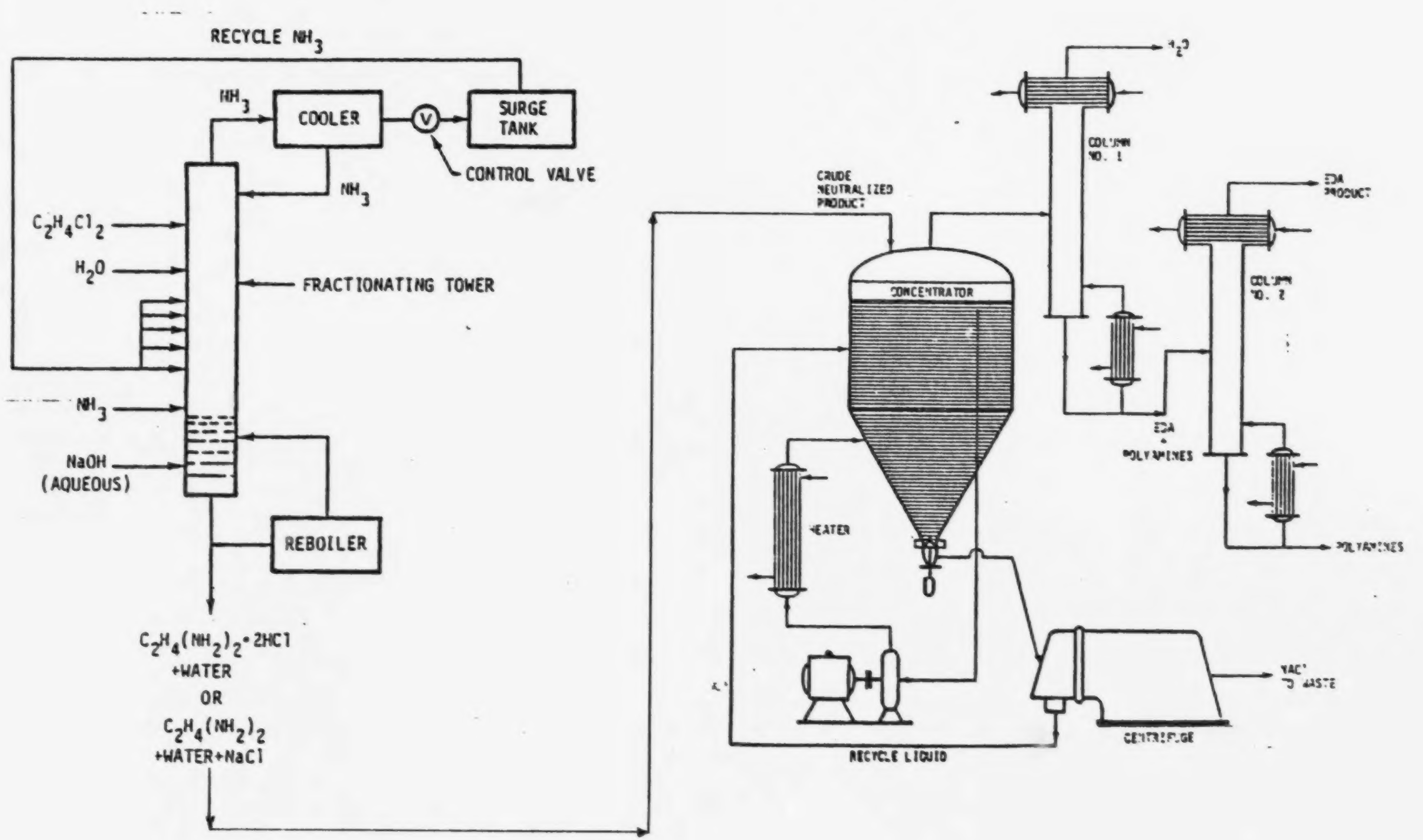
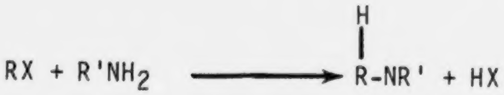
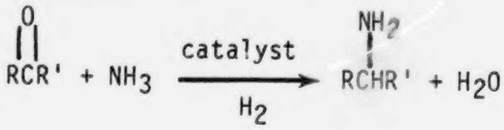


FIGURE 3-2 PROCESS FOR THE MANUFACTURE OF ETHYLENEDIAMINE FROM ETHYLENE DICHLORIDE AND AMMONIA.

SOURCE: HERRICK, ET AL 1979 b.

(1) 

$$RX + R'NH_2 \longrightarrow R\text{-}\overset{H}{\overset{|}{N}}R' + HX$$

(2) 

$$R\overset{O}{\overset{\|}{C}}R' + NH_3 \xrightarrow[H_2]{\text{catalyst}} R\overset{NH_2}{\overset{|}{C}}HR' + H_2O$$

There are four different ways in which ammonia behaves in ammonolytic reactions (Herrick et al. 1979b): double decomposition, dehydration, simple addition, and multiple activity. The first type of reaction to be discussed is double decompositon. This involves the NH_3 molecule splitting into $-NH_2$ and -H fragments. The $-NH_2$ becomes part of the new amine, and the -H joins with a radical like -Cl. Double decomposition is involved in the synthesis of ethylenediamine from ethylene dichloride:

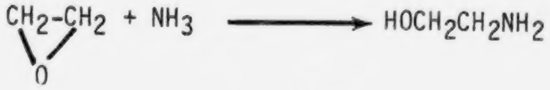
$$ClCH_2CH_2Cl + 2NH_3 \longrightarrow H_2NCH_2CH_2NH_2 + 2HCl$$

The second type of reaction is dehydration. Water and amines are produced by the ammonolysis of alcohols and by the hydroammonolysis of carbonyl compounds as the NH_3 acts as a hydrant. Synthesis of methylamines from methanol is an example of dehydration:

$$CH_3OH + NH_3 \xrightarrow{\text{catalyst*}} CH_3NH_2 + H_2O$$

*catalyst = alumina, clay, aluminum silicate

The third type of reaction is simple addition, in which both fragments, $-NH_2$ and -H, enter the new compound. Ammonia reacts with ethylene oxide to form ethanolamine in this way:



The fourth reaction forms secondary and tertiary amines by producing coreactants, the newly formed amines. They compete with NH_3 as a reactant. This type of ammonolytic reaction is known as multiple activity and occurs in the manufacture of methylamines:

$$CH_3OH + NH_3 \longrightarrow CH_3NH_2 + H_2O$$

$$CH_3OH + CH_3NH_2 \longrightarrow (CH_3)_2NH + H_2O$$

$$CH_3OH + (CH_3)_2NH \longrightarrow (CH_3)_3N + H_2O$$

The most common products of amination by ammonolysis are methylamines (mono-,di-, and tri-) from methanol; ethylamines (mono-, di-, and tri-) from ethanol; aniline from phenol; ethanolamines (mono-, di-, and tri-) from ethylene oxide; and ethylenediamine from ethanolamine and from ethylene dichloride (Herrick et al. 1979b). With the exception of the production of ethylenediamine from ethylene dichloride, the basic amination process involves reacting a mixture of an organic compound and ammonia in a reactor, usually catalytic, and separating the final product(s) from the reaction mixture (Figure 3-1). Ethylenediamine is formed from liquid aqueous ethylene dichloride in a fractionating column with liquid ammonia (Figure 3-2). No catalyst is involved. The final product is obtained by first introducing the amine mixture to a concentrator from which aqueous EDA and polyamine vapors are drawn off the top and separated.

3.2 DESCRIPTION OF DISCHARGES

Basically, all amination processes produce the same type of emissions. Feedstock excess ammonia that does not get recycled is always a discharge to be considered. Organic feestock that does not completely convert, approximately 1%, usually goes to waste and/or recycle. With a final yield of 95%, final product fugitive emissions and waste organic products from side reactions make up about 5% of the aminated products (Cocuzza et al. 1979, Habermann 1979, Klabunde 1979). Some of this may be recycled, but like the feedstocks, the exact amount that is emitted and does not get recycled is unknown. Also, solid catalyst fines are present in the wastewater of all amination processes except for ethanolamine and for ethylene diamine produced from ethylene dichloride, but the amount is unknown.

3.3 DESCRIPTION OF AN EXAMPLE PRODUCTION PROCESS: MANUFACTURE OF ETHANOLAMINES FROM THE AMINATION OF ETHYLENE OXIDE

This description of the manufacture of ethanolamines by the amination of ethylene oxide consists of four major steps: (1) amination reaction, (2)ammonia treatment: stripping and aqueous ammonia production, (3) dehydration, and (4) separation. Figure 3-3 illustrates this process. For each part, the description highlights the emissions associated with the step of the process.

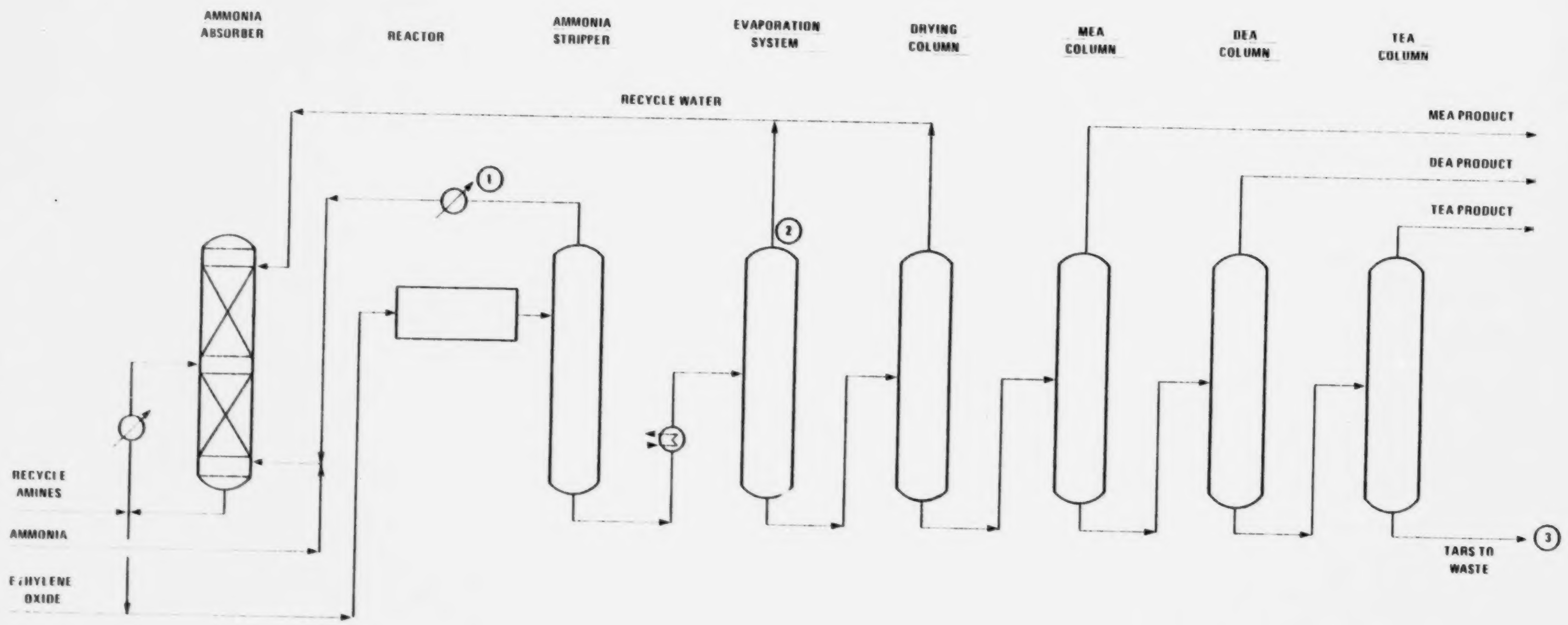


FIGURE 3-3 ETHANOLAMINES MANUFACTURE

SOURCE: HERRICK ET AL, 1979, p. 54

3.3.1 The Amination Reaction

Liquid ethylene oxide, aqueous ammonia in excess, and recycle amines are fed continuously to a coil-type reactor to produce ethanolamines. The exothermic liquid phase reaction takes place at moderate temperatures and pressures (50-100° C and 10-20 atm., respectively). The feed ratio is controlled to obtain the desired distribution of amines, mono-, di-, and tri-ethanolamine (Gruber 1975).

3.3.1.1 Emissions

Fugitive emissions may occur at valves, seals, and flanges.

3.3.2 Ammonia Treatment

The effluent from the reactor is pumped to an ammonia stripper where unreacted excess ammonia is removed under pressure as overhead. The bottoms from the stripper contain the crude ethanolamines. The excess ammonia from the overhead and the make-up ammonia are then fed to an ammonia absorber where water from the dehydrator is also fed to produce aqueous ammonia for the reactor (Gruber 1975).

3.3.2.1 Emissions

Nitrogen gas is passed from the stripper vent, as is some ammonia (100 ppm). Fugitive emissions may occur at valves, seals, and flanges (White 1980).

3.3.3 Product Dehydration

The bottoms of the ammonia stripper containing the ethanolamines are sent to an evaporator, operating at atmospheric pressure and 115° C. Excess water is removed as overhead and sent to the ammonia absorber to produce aqueous ammonia. The bottoms go to a dehydrator where, at 150 mm Hg and 140° C, the water content in the ethanolamines mixture is reduced to conform with specification limits. The water is removed as overhead and sent to aqueous ammonia production. The ethanolamines product exits the dehydrator as bottoms (Gruber 1975).

3.3.3.2 Emissions

Vents on the dehydrator purge gases that may enter the system (trace VOC). Fugitive emissions may occur at seals, valves, and flanges (White 1980).

3.3.4 Ethanolamines Separation

The dried ethanolamines are separated into three fractional distillation columns. Monoethanolamine, diethanolamine, and triethanolamine are removed as overhead from Columns 1, 2, and 3, respectively. The bottoms from the triethanolamine column are removed as a wastestream and are discharged to land disposal (Gruber 1975).

3.3.4.1 Emissions

The wastestream from the triethanolamine column contains TEA and tars of unknown composition and is considered hazardous (Gruber 1975). Fugitive emissions may occur at valves, pumps, and flanges.

3.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the ethanolamines manufacturing process (Table 3-2). The location of emissions source for Table 3-2 is found by consulting Figure 3-3. Releases are characterized as either routine (r) or accidental (a), controlled or uncontrolled.

Emissions data were found for the following two other amination by ammonolysis manufacturing processes:

Hexamethylene tetramine (Table 3-3)
Choline chloride (Table 3-4)

TABLE 3-2. CHARACTERIZATION OF EMISSIONS FROM THE ETHANOLAMINE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Nitrogen	impure feed	by-product	r	air	1[1]	NA	gas	NA	NA
Ethanolamines	vacuum jets	product	r	water	8[1]	NA	liquid	biological treatment	NA
Triethanolamine		product	r	land	40[2]	NA	liquid	NA	NA
Tars		by-product	r	land	40[2]	NA	solid	NA	NA
Bottoms product		by-product	r	land or incinerator	22[1]	NA	solid	NA	NA

[1] White, 1980, Vol. 9, Report 7, p. IV-1. based on 13, 600 kkg/yr capacity.

[2] Gruber, 1975, p. 5-21 - based on typical plant size of 14,000 kkg/year.

+Denotes that release is routine (r) or accidental (a).

TABLE 3-3. ESTIMATES RELEASES FROM THE HEXAMETHYLENETETRAMINE MANUFACTURING PROCESS

					Uncontrolled Emissions		Controlled Emissions		
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Formaldehyde	NA	feedstock	r	air/water	1.5	NA	gas, liquid	NA	NA
Methanol	NA	NA	NA	air/water	2.5	NA	gas, liquid	NA	NA
Ammonia	NA	feedstock	r	air/water	2.5	NA	gas, liquid	NA	NA
Hexamethylenetetramine	NA	product	r	air/water	NA	NA	gas, liquid	NA	NA
Nitrogen oxides	NA	NA	NA	air	NA	NA	gas	NA	NA

Source: EPA 1980. Organic Chemical Producers Database

+Emissions are routine (r)

TABLE 3-4. CHARACTERIZATION OF EMISSIONS FROM THE CHOLINE CHLORIDE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Trimethylamine	NA	feedstock	r	NA	1.5	NA	NA	NA	NA

Source: EPA 1980. Organic Chemical Producers Data Base.

+Emissions are routine (r).

REFERENCES

Cocuzza, G., and G. Torreggiani. 1979. Process for the Preparation and the Recovery of Ethanolamines. U.S. Patent 4,169,856.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. For Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Haberman, C. E. 1979. Method of Producing Amines from Alcohols, Aldehydes, Ketones, and Mixtures Thereof. U.S. Patent 4,153,581.

Herrick, E. C., J. A. King, and R. P. Ouellette, 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Herrick, E. C., J. A. King, R. P. Ouellette, and P. N. Cheremisinoff. 1979b. Amination Processes Pollutant Discharges Identification. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Klabunde, U. 1979. Preparation and Amination of Iodoaniline. U.S. Patent 3,975,439.

SRI International. 1981. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 9. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, N. C. EPA-450/3-80-028d.

Wilkins, G. E., C. H. Tucker, and E. D. Gibson. September 1980. The Revised Organic Chemical Producers Data Base. Prepared for the Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

SECTION 4 - AMMOXIDATION

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SECTION 4

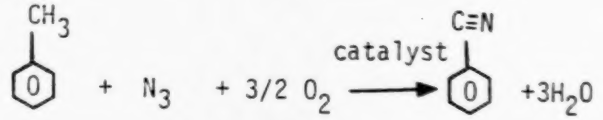
AMMOXIDATION

4.1 INTRODUCTION

In addition to acrylonitrile and benzonitrile, ammoxidation products include adiponitrile, hydrogen cyanide, phthalonitrile, isophthalonitrile, terephthalonitrile, and pyridine (Herrick et al. 1979a)(Table 4-1). The basic ammoxidation process (Figure 4-1) is carried out in a gas phase on a continuous basis. A heated tubular reactor, preferably a fluidized-bed-type, containing catalyst particles of antimony, molybdenum, or iron oxides is employed. The reaction occurs at high temperature, 350-550°C, atmospheric pressure, with a catalyst contact time of 0.4 to 5 seconds (Dalin et al. 1971). This reaction produces a mixture of nitriles of which hydrogen cyanide is very common. The desired nitrile must then be separated and purified. First, the reaction mixture enters a stripping column into which a solvent or sulfuric acid is introduced. The product exits this column as bottoms and is pumped into an absorber for "lights" removal, from which solvent and unwanted nitriles are removed as overhead gases. The product nitrile again exits as bottoms and is sent to a final distillation column where the pure product is obtained, usually as overhead, with heavies exiting into wastewater (Hosler et al.).

4.2 GENERAL CHEMISTRY

Ammoxidation is the process of forming nitriles by the reaction of ammonia in the presence of air or oxygen, with olefins, organic acids, or the alkyl group of alkylated aromatics (Herrick et al. 1979b). An example of ammoxidation is benzonitrile from toluene:



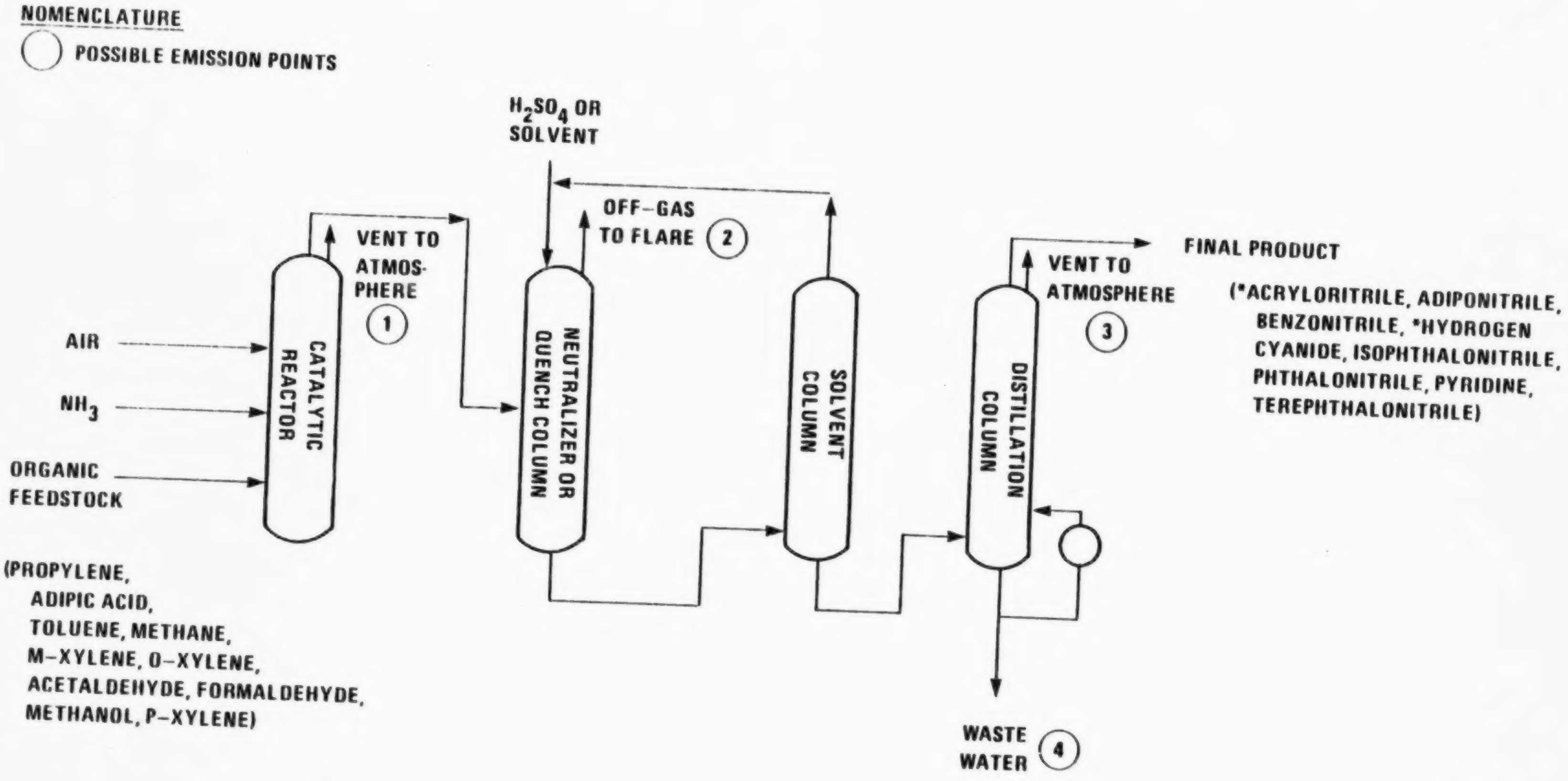
Nitriles' principal use is based on the fact that they undergo hydrolysis to form carboxylic acids (Dalin et al. 1971).

$$\begin{matrix} R\text{-}C\equiv N \\ \text{or} \\ Ar\text{-}C\equiv N \end{matrix} + H_2O \xrightarrow[\text{base}]{\text{acid or}} \begin{matrix} R\text{-}COOH \\ \text{or} \\ ArCOOH \end{matrix} + NH_3$$

TABLE 4-1
AMMOXIDATION PRODUCTS AND THEIR MANUFACTURE IN 1980

Product	Amount kkg	Feedstock	Other Required Processes
Acrylonitrile	760,221	propylene	
Adiponitrile	NA	adipic acid butadiene	halogenation
Benzonitrile	NA	toluene	
Hydrogen cyanide	439,803	methane	
Isophthalonitrile	NA	n-xylene	
Phthalonitrile	NA	o-xylene	
Pyridine, beta-picoline	NA	acetaldehyde formaldehyde methanol	condensation
Terephthalonitrile	NA	p-xylene	

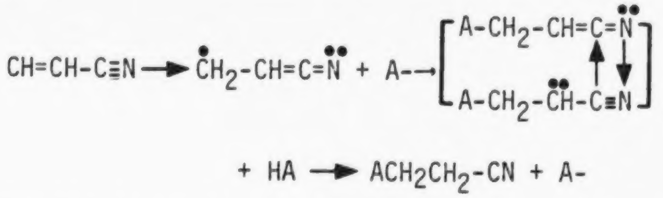
Source: Herrick et al. 1979a; SRI, 1981.


NOMENCLATURE
POSSIBLE EMISSION POINTS
AIR
NH_3
ORGANIC FEEDSTOCK
(PROPYLENE, ADIPIC ACID, TOLUENE, METHANE, M–XYLENE, O–XYLENE, ACETALDEHYDE, FORMALDEHYDE, METHANOL, P–XYLENE)
CATALYTIC REACTOR
VENT TO ATMOSPHERE
1
H_2SO_4 OR SOLVENT
NEUTRALIZER OR QUENCH COLUMN
OFF–GAS TO FLARE
2
SOLVENT COLUMN
DISTILLATION COLUMN
VENT TO ATMOSPHERE
3
FINAL PRODUCT
(*ACRYLORITRILE, ADIPONITRILE, BENZONITRILE, *HYDROGEN CYANIDE, ISOPHTHALONITRILE, PHTHALONITRILE, PYRIDINE, TEREPHTHALONITRILE)
WASTE WATER
4

*ACRYLONITRILE AND HYDROGEN CYANIDE ARE NEUTRALIZED WITH H_2SO_4 FOLLOWING REACTION; OTHER PRODUCTS ARE QUENCHED WITH A SOLVENT

FIGURE 4–1: GENERAL AMMOXIDATION PROCESS

The most common ammoxidation product is acrylonitrile from propylene:



$$CH=CH-C\equiv N \rightarrow \dot{C}H_2-CH=C=\ddot{N} + A- \rightarrow \left[\begin{array}{c} A-CH_2-CH=C=\ddot{N} \\ \uparrow\downarrow \\ A-CH_2-\ddot{C}H-C\equiv N \end{array}\right]$$

$$+ HA \rightarrow ACH_2CH_2-CN + A-$$

Acrylonitrile is used in the cyanoethylation of various organic compounds to form a beta-substituted propionitrile:

$$CH_2=CHCH_3 + NH_3 + 3/2\ O_2 \xrightarrow[\substack{400\text{-}510^\circ C \\ 1\text{-}2\ atm}]{catalyst} CH_2=CHC\equiv N + 3H_2O$$

These are used as plasticizers, emulsifiers, coatings, preparative chemicals, and fibers such as polyacrylonitrile (Dalin et al. 1971).

4.2 EMISSIONS

Table 4-2 summarizes the common emissions from ammoxidation processes of nitriles. Points of emission are indicated in Figures 4-1 and 4-2. In addition to feedstocks and product emissions, the hydrocarbon solvent added to the quench column usually contributes to reaction emissions. In the case of hydrogen cyanide and acrylonitrile productions, sulfuric acid is added to neutralize; this and the resulting side reaction forming ammonium sulfate add to the pollutants from the reaction section. Products from side reactions are also present in emissions. Other nitriles besides the desired product are usually formed, with hydrogen cyanide the most common. Carbon monoxide, carbon dioxide, and nitrogen oxides are also produced and released as off-gases (lights). Most of the off-gases go to an incinerator of greater than 99% efficiency or to recycle (Hydrocarbon Processing 1973); however, there can be leaks. Antimony, molybdenum, or iron particles may be found in the final wastewater because the catalyst is usually an oxide of one or a combination of these metals (Barnett et al., Doihyj et al., Hosler et al., Norton et al.).

TABLE 4-2. COMMON AMMOXIDATION EMISSIONS

Pollutant	Source
Organic feedstock	feedstock
Ammonia	feedstock
Product nitrile	product
Sulfuric acid	additive
Ammonium sulfate	side reaction
Hydrocarbon solvent	additive
Antimony	catalyst fines
Molybdenum	catalyst fines
Iron	catalyst fines
Hydrogen cyanide	side reaction
Carbon monoxide	side reaction
Carbon dioxide	side reaction
Nitrogen oxides	side reaction
Other nitriles	side reaction

4.3 DESCRIPTION OF AN EXAMPLE PRODUCTION PROCESS: Acrylonitrile Manufacture - The Ammoxidation of Propylene

The manufacture of acrylonitrile by the ammodixidation of propylene consists of four major steps: (1) acrylonitrile reaction, (2) quenching, (3) acrylonitrile recovery, and (4) acetonitrile recovery. Figure 4-2 illustrates this process. For each part, the description highlights the emissions associated with that step of the process.

4.3.1 Acrylonitrile Reaction

Propylene, ammonia, and air are fed continuously to a gas fluid-bed catalytic reactor, containing a solid antimony-uranium oxide catalyst. The reaction takes place in the vapor phase at temperatures of 400 to 510°C and relative low pressure of 1.4 to 3.1 atmospheres. In addition to acrylonitrile, the reaction produces hydrogen cyanide, acetonitrile, water, carbon monoxide, and propane (Gruber).

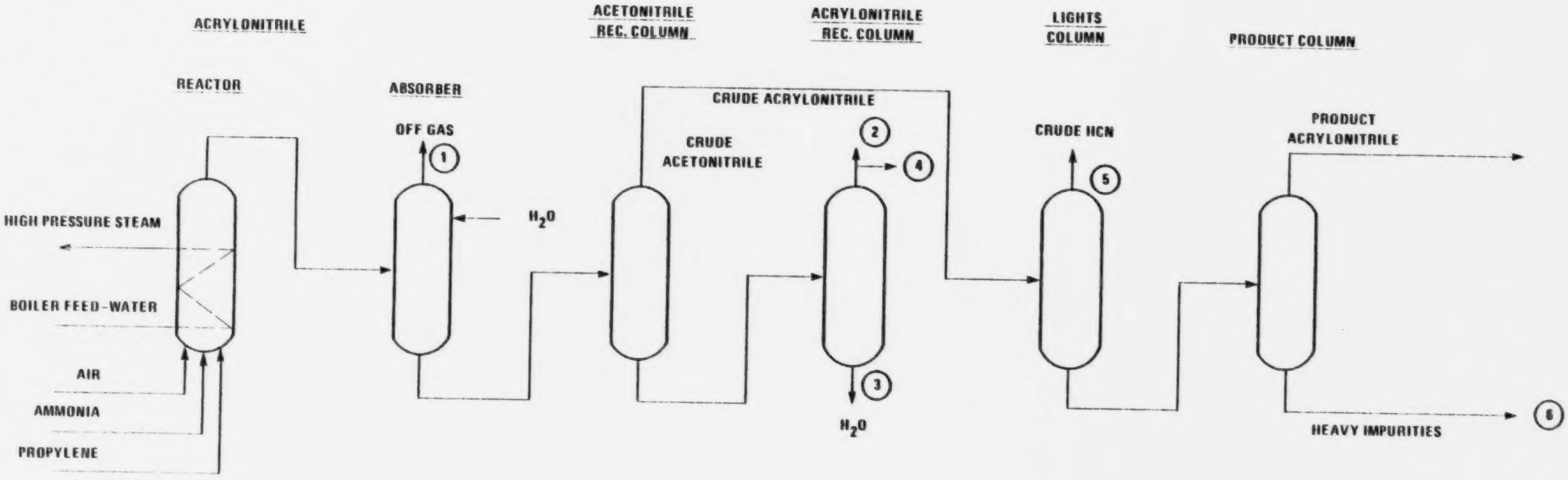


FIGURE 4-2: ACRYLONITRILE PROCESS

SOURCE: GRUBER, 1975. p. 5-43

4.3.1.1 Emissions

Fugitive emissions may occur from process pumps, compressors, and valves (White, p. C-1).

4.3.2 Quenching

The reactor effluent enters an absorber where it is scrubbed with water in a countercurrent flow. The off-gas contains mostly carbon monoxide, propylene, and propane.

4.3.2.1 Emissions

As a safety measure, the off-gas is flared before entering the atmosphere (Gruber 1975). Fugitive emissions may occur from pumps, compressors, and valves (White 1980). The bottoms, in solution with water, contain acrylonitrile, acetonitrile, hydrogen cyanide, and heavy ends (Gruber 1975).

4.3.3 Acrylonitrile Recovery

After quenching, the nitrile mixture exits the bottom of the absorber and enters a recovery column where wet acrylonitrile-hydrogen cyanide is removed as an overhead stream. This nitrile mixture is separated in a fractional distillation column, where crude HCN exits overhead and arylonitrile exits as bottoms to purification columns. In the final acrylonitrile distillation column, specification grade acrylonitrile is drawn off as overhead and heavy impurities (probably higher molecular weight nitriles and polymers) exit as bottoms (Gruber 1975).

4.3.3.1 Emissions

Fugitive emissions may occur from pumps and valves (White). The overhead hydrogen cyanide (HCN) from the HCN-acrylonitrile separation column contains light impurities which are flared. The heavy bottoms from the final column constitute a hazardous process waste which is sent to land disposal (Gruber, 1975).

4.3.4 Acetonitrile Recovery

The bottoms from the first acrylonitrile recovery column contain acetonitrile which enters a purification distillation column. Water leaves as bottoms and crude acetonitrile are drawn off as overhead where they enter a second distillation column (not shown). The overhead from this column contains HCN, which is flared, and acetonitrile. The bottoms from this column are heavy ends (probably nitrile polymers) (Gruber 1975).

4.3.4.1 Emissions

Fugitive emissions may occur from pumps and valves (White 1980). The water exiting the bottom of the first acetonitrile column contains some acetonitrile and goes to wastewater.

The heavy bottoms from the second acetonitrile distillation column constitute a hazardous process waste discharge to land (Gruber 1975).

4.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the acrylonitrile manufacturing process (Table 4-3). The location of emissions source for Table 4-3 is found by consulting Figure 4-2. Releases are characterized as either routine (r) or accidental (a), controlled or uncontrolled. Catalytic waste amounts were not available.

Emissions data have been found for two other ammoxidation manufacturing processes:

Benzonitrile (Table 4-4)
Hydrogen cyanide (Table 4-5)

TABLE 4-3. CHARACTERIZATION OF EMISSIONS FROM THE ACRYLONITRILE MANUFACTURING PROCESS

				Uncontrolled Emissions				Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Acrylonitrile	Absorber - 1	product	r	air (to flare)	0.1 - 5^2	2.05^2	gas	NA Thermal ozidizer	NA^3
	Column vents -2 and 5		r	air	5^2	103.00^2	gas	Flare	
	Seals, valves, flanges and drains		a	air	0.806^2	16.6^2	gas	Detection & correction of major leaks	$.001^3$ 0.05^3
Carbon monoxide	Absorber - 1	by-product	r	air (to flare)	200^2	NA	gas	NA	NA
Propane		by-product	r	air (to flare)	50^2	NA	gas	NA	NA
Propylene		feedstock	r	air (to flare)	100^2	NA	gas	NA	NA
Acetonitrile	Absorber - 1	by-product	r	air (to flare)	$trace^2$	NA	gas	NA	NA
	Acetonitrile recovery bottoms - 3		r	water	2^2	NA	liquid	NA	NA
Ammonia	Absorber - 1	feedstock	r	air (to flare)	$trace^2$	NA	gas	NA	NA
(NH) SO	Acetonitrile recovery-not shown	by-product	r	water	$unknown^1$	NA	liquid	NA	NA
Heavy ends	Acetonitrile recovery-not shown 2nd column bottoms-not shown	by-product	r	water	3^1	NA	liquid	NA	NA
	Final column - 6		r	land	2^1	NA	liquid	NA	NA
Hydrogen cyanide	Acetonitrile recovery 2nd column overhead - 4	by-product	r	air	1^1	NA	gas	NA	NA
Other VOC*	Absorber-1	by-product	r	air	99.9^2	2047.95^2	gas	Thermal oxidizer	0.999^3
	Column vents - 245		r	air	5^2	102^2	gas	Flare	0.05^3
	Seals, valves, flanges & drains		a	air	0.844^2	17.3^2	gas	Detection & correction of major leaks	0.249^3

TABLE 4-3. CHARACTERIZATION OF EMISSIONS FROM THE ACRYLONITRILE MANUFACTURING PROCESS (Cont'd)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Ammonia	NA	feedstock	r	water	12.[4]	NA	liquid	NA	NA
Ammonium acetate	NA	by-product	r	water	NA	NA	liquid	NA	NA
Ammonium acrylate	NA	by-product	r	water	NA	NA	liquid	NA	NA
Ammonium formate	NA	by-product	r	water	NA	NA	liquid	NA	NA
Ammonium methacrylate	NA	by-product	r	water	NA	NA	liquid	NA	NA
Benzonitrile	NA	by-product	r	water	NA	NA	liquid	NA	NA
Cadmium	NA	feedstock	r	water	.0003[4]	NA	liquid	NA	NA
Catalyst fines	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Chloride	NA	feedstock	r	water	.75[4]	NA	liquid	NA	NA
Chromium	NA	feedstock	r	water	.0002[4]	NA	liquid	NA	NA
Copper	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Cyanopyrazine	NA	NA	NA	water	NA	NA	liquid	NA	NA
Furonitrile	NA	by-product	r	water	NA	NA	liquid	NA	NA
Iron	NA	feedstock	r	water	.0065[4]	NA	liquid	NA	NA
Lutidine compounds	NA	NA	NA	water	NA	NA	liquid	NA	NA
Malononitrile	NA	by-product	r	water	NA	NA	liquid	NA	NA
Methacrylonitrile	NA	by-product	r	water	NA	NA	liquid	NA	NA
Methyl Pyrazine	NA	by-product	r	water	NA	NA	liquid	NA	NA
Nicotinonitrile	NA	by-product	r	water	.43[4]	NA	liquid	NA	NA
Nitrile	NA	by-product	r	water	.23[4]	NA	liquid	NA	NA
Oil and grease	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Organic Polymers	NA	by-product	r	water	NA	NA	liquid	NA	NA
Particulate	NA	by-product	r	air	.0035[4]	NA	gas	NA	NA
Phenol	NA	feedstock	r	water	.015[4]	NA	liquid	NA	NA
Phosphate	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Propionitrile	NA	by-product	r	water	NA	NA	liquid	NA	NA

TABLE 4-3. CHARACTERIZATION OF EMISSIONS FROM THE ACRYLONITRILE MANUFACTURING PROCESS (Cont'd)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Butane	NA	feedstock	r	air	.06[4]	NA	gas	NA	NA
Allyl alcohol	NA	feedstock	r	air	0.24[4]	NA	gas	NA	NA
Sulfur dioxide	NA	by-product	r	air	.017[4]	NA	gas	NA	NA
Nitrogen oxides	NA	by-product	r	air	.51[4]	NA	gas	NA	NA
Carbon monoxide	NA	by-product	r	air	200.0[4]	NA	gas	NA	NA
Methane	NA	feedstock	r	NA	.67[4]	NA	NA	NA	NA
Ethane	NA	feedstock	r	NA	.193[4]	NA	NA	NA	NA
Ethylene	NA	feedstock	r	NA	2.57[4]	NA	NA	NA	NA
Propane	NA	feedstock	r	NA	50.0[4]	NA	NA	NA	NA
Propylene	NA	feedstock	r	NA	100.0[4]	NA	NA	NA	NA
Butene	NA	feedstock	r	NA	.40[4]	NA	NA	NA	NA
Methanol	NA	feedstock	r	NA	.16[4]	NA	NA	NA	NA
Pentane	NA	feedstock	r	NA	.04[4]	NA	NA	NA	NA
Acetaldehyde	NA	by-product	r	NA	.06[4]	NA	NA	NA	NA
Hexane	NA	feedstock	r	NA	.04[4]	NA	NA	NA	NA
Ethanol	NA	feedstock	r	NA	.10[4]	NA	NA	NA	NA
Benzene	NA	feedstock	r	NA	.20[4]	NA	NA	NA	NA
Toluene	NA	feedstock	r	NA	.74[4]	NA	NA	NA	NA
Acrylonitrile	NA	product	r	Air	5.0[4]	NA	gas	NA	NA
Acetonitrile	NA	by-product	r	Air	.68[4]	NA	gas	NA	NA
Hydrogen cyanide	NA	by-product	r	Air	1.0[4]	NA	gas	NA	NA
Fumaronile	NA	NA	NA	Air	.018[4]	NA	gas	NA	NA
Propionaldehyde	NA	feedstock	r	NA	.006[4]	NA	NA	NA	NA
Furan	NA	by-product	r	Air	.47[4]	NA	gas	NA	NA
Pyridine	NA	NA	NA	NA	2.2[4]	NA	NA	NA	NA

TABLE 4-3. CHARACTERIZATION OF EMISSIONS FROM THE ACRYLONITRILE MANUFACTURING PROCESS (Cont'd)

Pollutant	Location	Source	Type of Release†	Receiving Medium	Uncontrolled Emissions			Controlled Emissions	
					Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Pyrazine	NA	by-product	r	water	NA	NA	liquid	NA	NA
Pyrazole	NA	by-product	r	water	NA	NA	liquid	NA	NA
Succinonitrile	NA	by-product	r	water	NA	NA	liquid	NA	NA
Sulfate	NA	feedstock	r	water	34.1[4]	NA	liquid	NA	NA
Ticoline	NA	NA	NA	water	NA	NA	liquid	NA	NA
Trans-crotonitrile	NA	by-product	r	water	NA	NA	liquid	NA	NA
Wastewater	NA	scrubber	r	water	4470.0[4]	NA	liquid	NA	NA
Zinc	NA	feedstock	r	water	.0045[4]	NA	liquid	NA	NA
Ammonia	NA	feedstock	r	air	.000006[4]	NA	gas	NA	NA
Acetaldehyde cyanohydrin	NA	by-product	r	water	NA	NA	liquid	NA	NA
Acetic acid	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Acetone cyanohydrin	NA	by-product	r	water	NA	NA	liquid	NA	NA
Acetone	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Acrolein cyanohydrin	NA	by-product	r	water	NA	NA	liquid	NA	NA
Acrolein	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Acrylamide	NA	by-product	r	water	NA	NA	liquid	NA	NA
Acrylic acid	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Allyl cyanide	NA	by-product	r	water	NA	NA	liquid	NA	NA
Ammonium sulfate	NA	feedstock	r	water	NA	NA	liquid	NA	NA

[1] Gruber, 1975, p. 5-43, based on 4500-160,000 kkg/year.

[2] White, 1980, Vol. 10, Report 2, p. IV-3, based on 180,000 kkg/yr

[3] Ibid, p. V-2.

[4] EPA, 1981, Organic Chemical Producers Data Base.

† Denotes that release is routine (r) or accidental (a).

* May include acetonitrile, propane, propylene, carbon monoxide hydrogen cyanide.

TABLE 4-4. CHARACTERIZATION OF EMISSIONS FROM THE BENZONITRILE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release†	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kgg product
Benzene	NA	feed impurity	r	air	1.0	NA	gas	NA	NA
Ammonia	NA	feedstock	r	air	1.0	NA	gas	NA	NA
Hydrogen cyanide	NA	feed impurity	r	air	NA	NA	gas	NA	NA
Toluene	NA	feedstock	r	air	NA	NA	gas	NA	NA

Source: EPA, 1981, Organic Chemical Producers Data Base.

†Emissions are routine (r).

TABLE 4-5. CHARACTERIZATION OF EMISSIONS FROM THE HYDROGEN CYANIDE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Methane	ammonia and HCN absorbers	feedstock	r	air	8.5	NA	gas	NA	NA
Nitrogen		feedstock	r	air	8228.2	NA	gas	NA	NA
Hydrogen		feedstock	r	air	829.0	NA	gas	NA	NA
Hydrogen cyanide		product	r	air	6.2	NA	gas	NA	NA
Carbon dioxide		feedstock	r	air	70.3	NA	gas	NA	NA
Carbon monoxide		feedstock	r	air	581.3	NA	gas	NA	NA

Source: Pervier et al. 1974.

+Emissions are routine (r).

REFERENCES

Barnett, C., and J. Dewing. Process for the Preparation of Adiponitrile by the Ammoxidation of Cyclohexane. U.S. Patent 3,818,066.

Dalin, M. A., I. K. Kolchin, and B. R. Serebryakov. 1971. Acrylonitrile. Westport, Connecticut: Technomic Publishing Co., Inc.

Doihyj, S. R., and L. J. Velenyl. Process for Producing Pyridine or a Substituted Pyridine by Ammoxidation of Terpenes. U. S. Patent 4,140,690.

Gruber, G. I., TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. For Environmental Protection Agency. Office of Solid Waste. Washington, D.C. EPA/530/SW-118C.

Herrick, E. C., J. A. King, and R. P. Quellette. 1979a. Unit Process Guide to Organic Chemicals Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Hosler, P., and R. A. Baillie. Separation of Liquid Isophthalonitrile. U. S. Patent 3,801,620.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Morrison, R. T., and R. N. Boyd. 1973. Organic Chemistry, 3rd ed. Boston, Massachusetts: Allyn and Bacon, Inc.

Pervier, J. W. et al. April 1974. Survey Reports on Atmospheric Emissions from the Petrochemical Industry (2 volumes). USEPA/OAPQS, Research Triangle Park, North Carolina, EPA-450/3-73-005A&B.

Norton, R. V., and R. D. Bushick. Terephthalonitrile Process. U. S. Patent 3,862,202.

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 10. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028e.

REFERENCES (continued)

Wilkins, G. E., C. H. Tucker, and E. D. Gibson. September 1980. The Revised Organic Chemical Producers Data Base. Prepared for the Environmental Protecton Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

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SECTION 5

CARBONYLATION

5.0 INTRODUCTION

Carbonylation is the addition of carbon monoxide to an organic compound. Small carboxylic acid, alcohols, and aldehydes are prepared by carbonylation. Hydrogenation generally follows carbonylation to supply the additional hydrogen needed to make acids and alcohols from aldehydes. Table 5-1 lists the organic chemicals manufactured by carbonylation (Herrick 1979) and their amounts produced in 1981 (SRI 1981). Most carbonylation reactions occur at high pressures to keep the carbon monoxide in the liquid state. The main environmental concern will be gaseous emissions of carbon monoxide and volatile organic compounds.

Carbonylation processes generally follow a process sequence of 1) compression, 2) carbonylation reaction, 3) cooling, 4) purification, and 5) separation. Most reactions are catalytic and occur at high pressures. Typical catalysts are halogenated acetate salts or halogenated carbonyl forming metals (iron, cobalt, rhodium, or nickel). Figure 5-1 is a flow diagram for a typical carbonylation process.

5.1 GENERAL CHEMISTRY

Carbonylation reactions occur most often when &-olefins are reacted with carbon monoxide to form aldehydes or alcohols. The resulting aldehyde/alcohol has one more carbon atom than the starting &-olefin, which comes from the carbon monoxide. This type of carbonylation is called an oxo reaction, and the products are referred to as the oxo chemicals. An &-olefin is a hydrocarbon with a double bond between the first and second carbon atoms. Reaction 1 demonstrates the oxo reaction (using the BASF AG process) which makes n-butyraldehyde from propylene, carbon monoxide and hydrogen. It is performed at 270 to 300 atm of pressure to keep the carbon

TABLE 5-1. CARBONYLATION PRODUCTS AND THEIR MANUFACTURE IN 1980

Product[1]	Amount kkg	Feedstock[1]	Other Required Processes[1]
Acetic Acid	565,526[2]	Methanol Carbon Monoxide	None
Alcohols (C_7-C_{13})	NA[3]	Olefins Carbon Monoxide	None
n-Butanol/ n-Butyraldehyde	413,681[4] 488,070[4]	Propylene Carbon Monoxide	Hydrogenation
Ethyl acrylate	NA[3]	Acetylene Ethanol Carbon Monoxide	None
2-Ethyl hexanol/ n-Butyl alcohol	125,193[4] same as n-Butanol	Propylene Carbon Monoxide	Hydrogenation
Isobutyraldehyde/ Isobutyl alcohol	118,298[4] 98,340[4]	Propylene Carbon Monoxide	Hydrogenation
Formic acid Sodium formate	 27,216[4]	Carbon Monoxide Sodium Hydroxide	Hydrolysis
Formic Acid		Carbon Monoxide (Methanol Recycled)	Condensation Hydrolysis

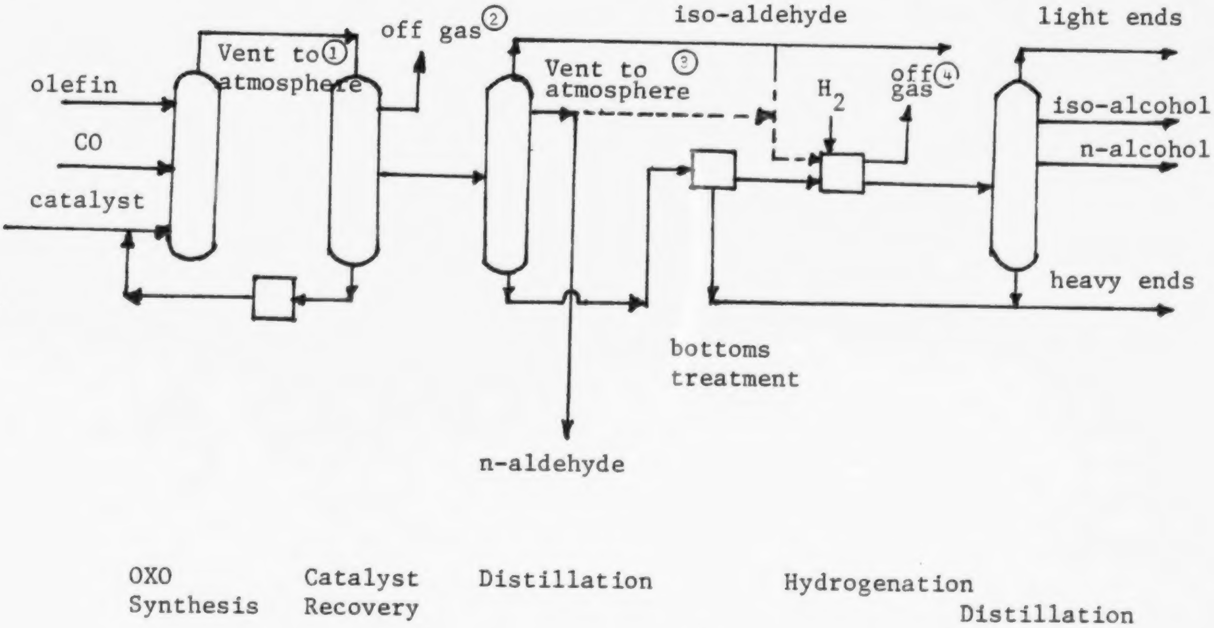
[1] Source: Herrick et al. 1979.

[2] Source: SRI 1981.
Assumes 80% of capacity is produced.
Kirk-Othmer (1980) states that 34 to 37% of all acetic acid is manufactured by methanol carbonylation. This value is 35.5% of the total.

[3] Source: SRI 1981.
Does not give amounts produced, but lists producers.

[4] Source: SRI 1981
Assumes that 80% of capacity is produced and also assumes that the amount produced was by carbonylation. Capacities may include corresponding iso- or n- compounds; for example the amount of n-butyraldehyde produced may include iso-butyaldehyde.

FIGURE 5-1. A TYPICAL CARBONYLATION PROCESS.



Nomenclature

O Possible Emissions Points

Source: Adopted from Hydrocarbon Processing, 1973.

monoxide in the liquid state. Alcohols are formed when an excess of hydrogen is present. A cobalt catalyst is used for the carbonylation reaction, and a nickel catalyst is used for the succeeding hydrogenation reaction.

$$\underset{\text{propylene}}{CH_2{=}CHCH_3} + CO + H_2 \xrightarrow[\substack{160\text{-}175^\circ C \\ 270\text{-}300 \text{ atm}}]{\text{Cobalt catalyst}} \underset{\text{n-butyraldehyde}}{CH_3CH_2CH_2CHO} \qquad (1)$$

$$CH_3CH_2CH_2CHO + H_2 \xrightarrow{\text{nickel}} \underset{\text{n-butanol}}{CH_3CH_2CH_2CH_2OH}$$

Acetic acid is the carbonylation chemical with the largest production volume. In the Monsanto process, it is formed by reacting methanol with hydrogen and carbon monoxide in the presence of a soluble rhodium iodocarbonyl catalyst. The catalyst is dissolved in the methanol and introduced as a liquid solution. The hydrogen and carbon monoxide are reacted in the gaseous state. The reaction proceeds as follows:

$$\underset{\text{methanol}}{CH_3OH} + CO(g) \xrightarrow[\substack{175^\circ C \\ 30 \text{ atm}}]{\text{Rhodium catalyst}} \underset{\text{acetic acid}}{CH_3COOH} \qquad (2)$$

5.2 DESCRIPTION OF DISCHARGES

Releases from a carbonylation process will occur as fugitive and particulate gaseous emissions, liquid wastes, and solid residues. The major sources of contamination are gaseous emissions from the vents on the reactors which pull off the gaseous by-products and solid emissions resulting from the disposal of the bottoms product from the heavy ends distillation column.

fugitive gaseous emissions	may occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains, and cooling towers.
compression	fugitive emissions will occur, especially at compressor seals. liquid wastes will result when flushing the compressors and when the oil used to grease the compressors leaks out.
carbonylation reactor	pollutants will be released from the off-gas vent on the reactor.
cooling and condensing	condensers, partial condensers, and heat exchangers cause contaminated liquid waste streams and vent gases.
purification	gas scrubbers, degassers, and water washes create large contaminated liquid waste streams and large gaseous waste streams.
product separation	distillation columns (both conventional and extractive distillation) cause fugitive and intermittent air emissions, solid bottoms products to be disposed, and contaminated liquid wastes containing products and extractive solvents.
steam generation and cooling tower operation	contaminants are released during operation and at blowdown.

All carbonylation reactions release volatile organic compounds (VOCs). VOCs include organic chemicals which, when emitted to the atmosphere, participate in photochemical reactions producing ozone. VOCs are emitted not only to the air, but also to the land and water.

5.3 PRODUCTION PROCESS - ACETIC ACID BY CARBONYLATION

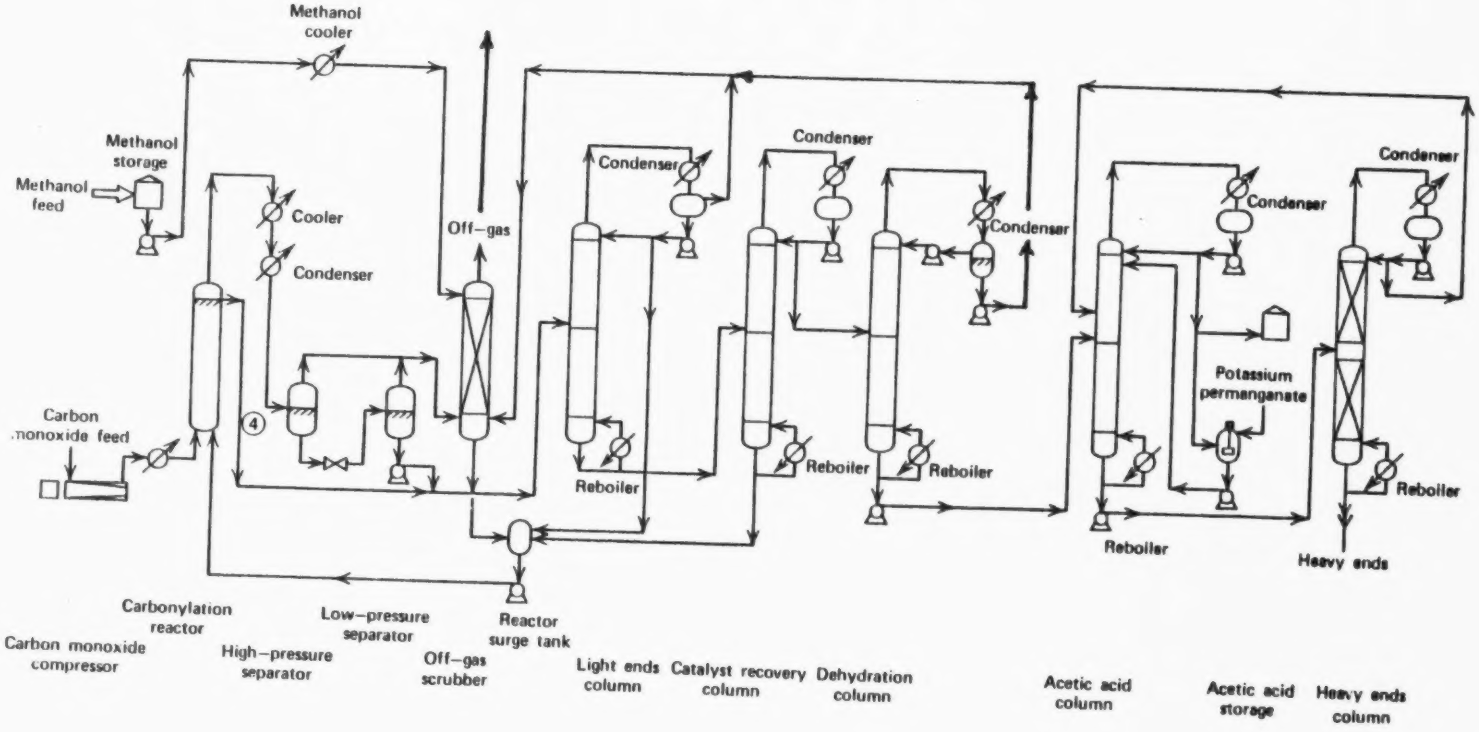
The carbonylation chemical with the largest production volume is acetic acid. n-Butyraldehyde is ranked second in production volume, most of which undergoes aldol condensation and hydrogenation to make 2-ethylhexanol. The following discussion on the production of acetic acid by carbonylation will include the VOC emission points. Most of the information in this production process section was gained from Kirk-Othmer (1980), USEPA (1980), and Shreve (1967). Figure 5-2 is a detailed flow diagram of the BASF carbonylation process used to make acetic acid.

Acetic acid is produced by a continuous, liquid-phase, catalytic reaction of methanol and carbon monoxide. Although processing schemes may vary, the processing sequence for the production of acetic acid is generally 1) a reaction system, 2) a scrubber system, and 3) a distillation system (5 distillation columns). First, liquid methanol, liquid carbon monoxide, and a dissolved catalyst are fed to a tubular reactor which is operating at 150 to 200°C and a pressure of 33 to 65 atm. The crude liquid product is sent to the distillation system to separate out a pure product. The distillation system consists of a light ends column, a catalyst recovery column, a dehydrator, an acetic acid column, and a heavy ends column. Most of the non-product streams from these columns are recycled to the reactor. Gases vented from the reactor system and the distillation system are combined and sent to a scrubber system where they are recovered and recycled to the reactor. Very little waste is generated because almost everything is recycled to the reactor. The unwanted gases from the scrubber system are sent to a flare, and the bottoms from the heavy ends column are sent to be incinerated.

5.3.1 Carbonylation Reactor

Methanol and carbon monoxide are fed to a continuous, tubular reactor which operates at 150 to 200°C and a pressure of 33 to 65 atm. The liquid methanol feed first goes from storage through a cooler and to the vent gas scrubber, where it is used as the washing liquid. The methanol feed is combined with recycle in a reactor surge tank and then pumped to the reactor. Catalysts, usually cobaltous iodide or rhodium iodide, are dissolved in water and added to the reactor. The crude acetic acid product is formed after a reaction time of 1 to 3 minutes. Water and other impurities are formed from side reactions. These impurities include gases such as hydrogen, methane, nitrogen, carbon dioxide and carbon monoxide, and liquid by-products such as dimethyl ether, methyl acetate, acetaldehyde,

FIGURE 5-2. A TYPICAL METHANOL CARBONYLATION FLOW SHEET.



Source: Kirk-Othmer, 1980.

butyraldehyde, ethyl acetate propionic acid, and higher organics. The by-product gases are vented to the scrubber system. The liquid by-products are separated out in the distillation system.

The feed methanol is diluted with water to prevent methyl acetate from forming. One of the side reactions that occurs is the water-gas reaction where water reacts with carbon monoxide to form carbon dioxide and hydrogen. Therefore, the water must be carefully monitored to keep the water-gas reaction from predominating. Water is used to clean the reactors; therefore, diluted acid and other hydrocarbons will be drained off.

5.3.1.1 Emissions from Carbonylation Reactor

The largest emission from the carbonylation reactor would be the off-gases from the reactor vent; however, these are being circulated through the vent gas scrubber and recycled to the reactor. Fugitive emissions will occur from leaks, valves, and flanges in the reaction equipment and during storage of the feedstocks. A water waste stream will result when the equipment is cleaned. The catalysts are reused but not regenerated, so it is not necessary to review regenerating waste.

5.3.2 Off-gas Scrubber System

The off-gases from the vent on the reactor and the vents on the distillation columns are sent to the scrubber system. The vent gases from the reactor are first cooled and condensed and sent through two vapor-liquid separators. The liquid from the separators is mixed with the liquid products from the reactor and sent to the distillation system. The gases from the separators proceed to the off-gas scrubber. Constituents of the vent gases include methyl iodide, methane, hydrogen, water vapor, nitrogen, carbon monoxide, and carbon dioxide. The purpose of the off-gas scrubber is to recover the unreacted catalyst gas, methyl iodide, by washing it with the methanol feed. Iodine and water are absorbed by this methanol and are sent to the reactor surge tank without any further treatment. The waste gases--methane, hydrogen, nitrogen, carbon monoxide, and carbon dioxide--go to a flare, which is 98.5% efficient (USEPA 1980).

5.3.2.1 Emissions from the Off-gas Scrubber System

The majority of emissions from the off-gas scrubber system are those from the flare. USEPA (1980) reports that the flares are 98.5% efficient and that 0.356 kg of carbon monoxide/kkg of acetic acid is emitted and 0.03 kg of acetic acid/kkg of acetic acid is emitted. EPA has also observed that for the same 22.7 kkg/hr (50,000 lb/hr) plant, halogen compounds leave the flare at a rate of 0.45 to 0.9 kg/hr (1 to 2 lbs/hr). Table 5-2 shows the estimated composition of the gas from the reactor vent in a BASF plant (USEPA 1980) before it enters the scrubber system. Table 5-3 shows the estimated gas composition exiting from the light ends distillation vent before it reaches the scrubber or the flare. These gases all have the potential to be emitted from the flare; however, numbers were only calculated for acetic acid and carbon monoxide.

The cooling water in the coolers and condensers may become contaminated with the chemicals listed in Table 5-2. Fugitive emissions, both gaseous and liquid, are known to occur from vapor-liquid separators. Fugitive emissions may also occur from the off-gas scrubber.

5.3.3 Distillation System - Light Ends Column

The crude liquid acetic acid product from the reactor contains many impurities. These include catalyst residues, water, low boiling organics, and heavy residues. The light ends distillation column separates the low boiling organics from the crude acetic acid. The low boiling organics are mainly dimethyl ether, methyl acetate, acetaldehyde, butyraldehyde, and ethyl acetate. These emerge in the overhead vapors and are partially condensed after which the liquid and vapors are separated. The overhead liquid is recycled to the reactor, and the overhead vapors are sent to the off-gas scrubber. The bottoms product containing the acetic acid is sent to the catalyst recovery column.

5.3.3.1 Emissions from the Light Ends Column

Fugitive emissions of hydrocarbons may result from seals, valves, and leaks in the entire fractionation train, which includes the

TABLE 5-2. ESTIMATED COMPOSITION OF GAS FROM REACTOR OFF-GAS SCRUBBER VENT IN A BASF METHANOL CARBONYLATION PLANT PRODUCING ACETIC ACID[a]

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Methanol	3.5	12.9
Light ends	0.6	2.1
Total VOC	4.1	15
Hydrogen	1.5	5.5
Carbon monoxide	54	204
Carbon dioxide	37	141
Methane	3.4	12.8
Total	100	378

[a] Based on a theoretical material balance

[b] g of emissions per kg of acetic acid produced.

Source: USEPA (1980).

TABLE 5-3. ESTIMATED GAS COMPOSITION OF LIGHT-ENDS DISTILLATION COLUMN VENT IN A BASF METHANOL CARBONYLATION PLANT TO PRODUCE ACETIC ACID

Component	Composition (wt %)	Emission Ratio (g/kg)[b]
Hydrogen	0.28	0.079
Carbon monoxide	30	8.59
Carbon dioxide	67.5	19.3
Methane	2.22	0.63
Total	100	28.6

[a] Based on a theoretical material balance

[b] g of emissions per kg of acetic acid produced.

Source: USEPA (1980).

reboiler, condenser, and light ends column. Intermittent emissions may result from the relief vents on the column.

5.3.4 Distillation System - Catalyst Recovery Column

In the catalyst recovery column, the crude acetic product is freed from cobaltous iodide or rhodium iodide, depending on the original catalyst used. This column is operated as an atmospheric flash column. The catalysts are removed from the column in an aqueous acetic solution as the bottoms product and recycled to the reactor surge tank. The acetic acid proceeds as the overhead to the dehydrator.

5.3.4.1 Emissions from the Catalyst Recovery Column

Fugitive emission of VOCs may occur at seals, valves, and leaks in the fractionation train. Intermittent emissions may result from the relief vents on the columns. No catalyst sludge is expected since it is in solution with the acetic acid and recycled to the reactor.

5.3.5 Distillation System - Dehydration Column

The purpose of the dehydration column is to separate the water from the acetic acid. This separation is impractical by conventional distillation since the boiling points are so close; therefore, azeotropic distillation using an entrainer is employed. The entrainer is a water-insoluble, water-withdrawing liquid which for this distillation is a steam/volatile by-product mixture from the first vapor-liquid separator before the off-gas scrubber. The entrainer distills together with the water as a minimum boiling azeotrope and exits as an overhead stream. The overhead vapors are condensed and passed through a decanter. The entrainer from the top of the decanter is returned to the column. The water is drawn off the bottom of the decanter and is recycled to the off-gas scrubber. The bottoms product from the dehydration column is dried acetic acid and is sent to the acetic acid column.

5.3.5.1 Emissions from the Dehydration Column

Fugitive emissions of hydrocarbons and water may occur at seals, valves, and leaks in the fractionation train. Intermittent emissions may result from the relief vents on the column.

5.3.6 Distillation System - Acetic Acid Column and Heavy Ends Column

In the acetic acid column, the acetic acid is separated from the heavy residues. The acetic acid product passes as the overhead vapors and is condensed and sent to storage. The heavy residues consist of 50% propionic acid and 50% higher organics. (Hedley 1975). The heavy residues are passed as the bottoms product to the heavy ends column. The heavy ends column recirculates any light organics back to the acetic acid column. The bottoms of the heavy ends column according to Hedley (1975) is 40 kg of heavy residue per kkg of acetic acid in a 1:1 ratio of propionic acid to higher organics. The propionic acid and higher organics, i.e., heavy residue, are incinerated (USEPA 1980).

5.3.6.1 Emissions from Acetic Acid Column and Heavy Ends Column

Fugitive emissions of hydrocarbons may result from seals, valves, and leaks in both fractionation trains. Intermittent emissions may result from the relief vents on the columns. If the incineration of the heavy residues is incomplete, an air emission of higher organic chemicals will occur.

5.4 SUMMARY OF EMISSION DATA

Table 5-4 shows major sources of emissions and amounts released as estimated by Hedley (1975) and USEPA (1980). Figures 5-3 and 5-4 show the flow diagrams of n-butanol and 2-ethylhexanol being made by carbonylation. Points of emissions are demonstrated on each figure.

These data and figures outline the basic processes and emission points for a carbonylation process. Individual process wastes will differ depending on the operating conditions, volatilities, and solubilities of

TABLE 5-4. CHARACTERIZATIONS OF EMISSIONS FROM CARBONYLATION PROCESSES

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Acetic acid[1]	-hydrogen	reaction section-off-gas scrubber vent	by-products	r	air	5.5[2]	NA	gas	flare	NA
	carbon monoxide					204[2]	NA	gas		0.356[3]
	methane					12.8[2]	NA	gas		NA
	methanol					12.9[2]	NA	gas		NA
	light ends					2.2[2]	NA	gas		NA
	acetic acid					NA	NA	gas		0.03[3]
	halogens		catalysts			NA	NA	gas		0.04[3]
	-propionic acid	bottoms product of heavy ends column	by-products	r	land	20[2]	NA	solid	Incinerated	NA
	higher organics					20[2]	NA	solid		NA
	-volatile organic compounds (VOC)	entire carbonylation process (250,000 Mg/yr capacity	by-products	r	air	2[3]	57[3]	gas	flare	0.02[3]
Ethyl acrylate[4]	-acetylene	off-gas from the reactor after passing through an ethanol scrubber	reactants	r	air	6.1[2]	NA	gas	NA	NA
	carbon monoxide					6.1[2]	NA	gas	NA	NA
	-sodium carbonate	wastewater from the neutralizer	by-products	r	water	11.4[2]	NA	liquid	NA	NA
	sodium acrylate					43.2[2]	NA	liquid	NA	NA
	-polymers	heavy end from the ethyl acrylate purification section	by-products	r	land	33.6[2]	NA	solid	NA	NA
	hydroquinone					13.0[2]	NA	solid	NA	NA
	-nickel chloride	effluent from knock out drum of carbonyl preparation section	impurities	r	land	0.8[2]	NA	solid	NA	NA
	sodium hydroxide					4.0[2]	NA	solid	NA	NA
	sodium carbonate					58.3[2]	NA	solid	NA	NA
	sodium sulfide					3.5[2]	NA	solid	NA	NA
	sodium chloride					63.0[2]	NA	solid	NA	NA
	-ethanol	bottoms from alcohol dehydrator	by-products	r	water	4.8[2]	NA	liquid	NA	NA

TABLE 5-4. CHARACTERIZATION OF EMISSIONS FROM CARBONYLATION PROCESSES
(continued)

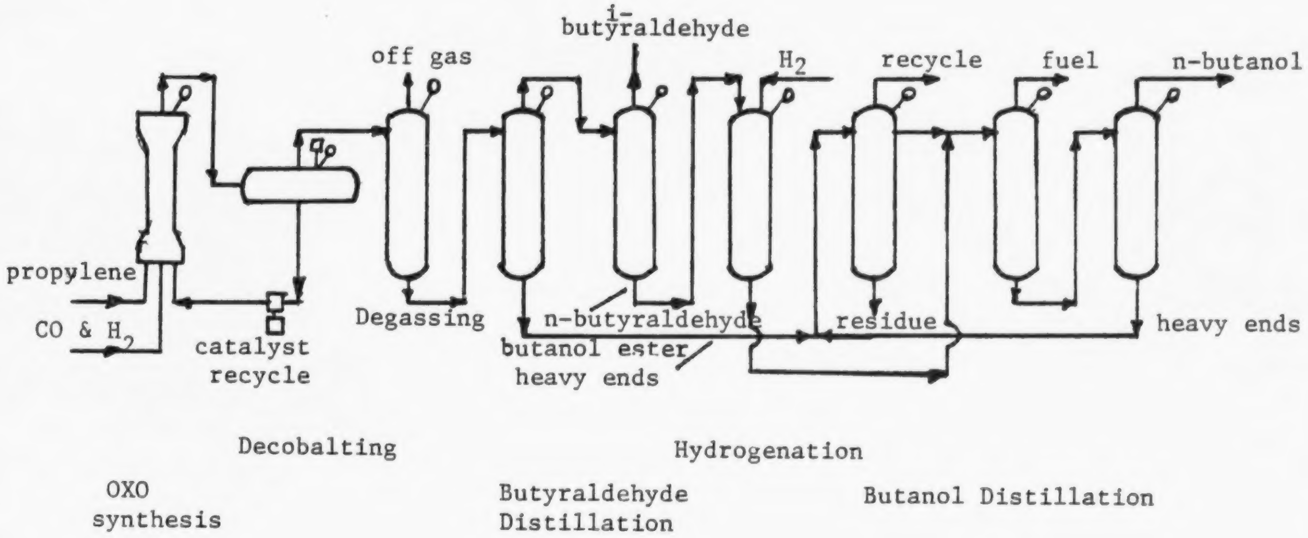
						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
n-Butyraldehyde	-carbon monoxide	catalyst recovery system	catalysts &	r	air/water	NA[2]	NA	gas	NA	NA
	propylene	air vent discharge or	by-products			NA[2]	NA	or	NA	NA
	propane	wastewater discharge				NA[2]	NA	liquid	NA	NA
	-heavy ends	incinerated	by-products	r	air	NA[2]	NA	gas	NA	NA
	-light ends	flared	by-products	r	air	NA[2]	NA	gas	NA	NA
n-Butanol	-hydrogen	hydrogenation of	by-products	r	air	NA[2]	NA	gas	NA	NA
	organic vapors	n-butyraldehyde				NA[2]	NA	gas	NA	NA
		hydrogenation reactor vent				NA[2]	NA	gas	NA	NA
2-Ethyl hexanol[5]	-butyraldehyde	sodium hydroxide recovery section, water evaporator	reactants	r	air	55.9[2]	NA	gas	NA	NA
	-light hydrocarbons	light ends stripper	by-products	r	air	114[2]	NA	gas	NA	NA
	-heavy ends	bottoms of 2-ethyl hexanol column	by-products	r	land	NA[2]	NA	solid	Incinerated	NA

The emissions from the carbonylation of oxo mixed linear alcohols will be similar to the releases during the production of n-butanol from n-butyraldehyde which came from propylene and carbon monoxide. The reaction conditions will vary. Air pollution by organic vapors will be less (not as volatile) while other types of pollution should be the same (Hedley 1975).

[1] Basis: 45,400 kkg/yr (100 $\overline{M}$ lb/yr) capacity.
[2] Source: Hedley et al. 1975.
[3] Source: USEPA 1980.
[4] Basis: 13,600 kkg/yr (30 $\overline{M}$ lb/yr) capacity.
[5] Basis: 22,700 kkg/yr (50 $\overline{M}$ lb/yr) capacity.

+ If emissions are routine (r) or accidental (a).

FIGURE 5-3. MANUFACTURE OF n-BUTANOL BY CARBONYLATION AND HYDROGENATION.



Source: Hydrocarbon Processing, 1973.

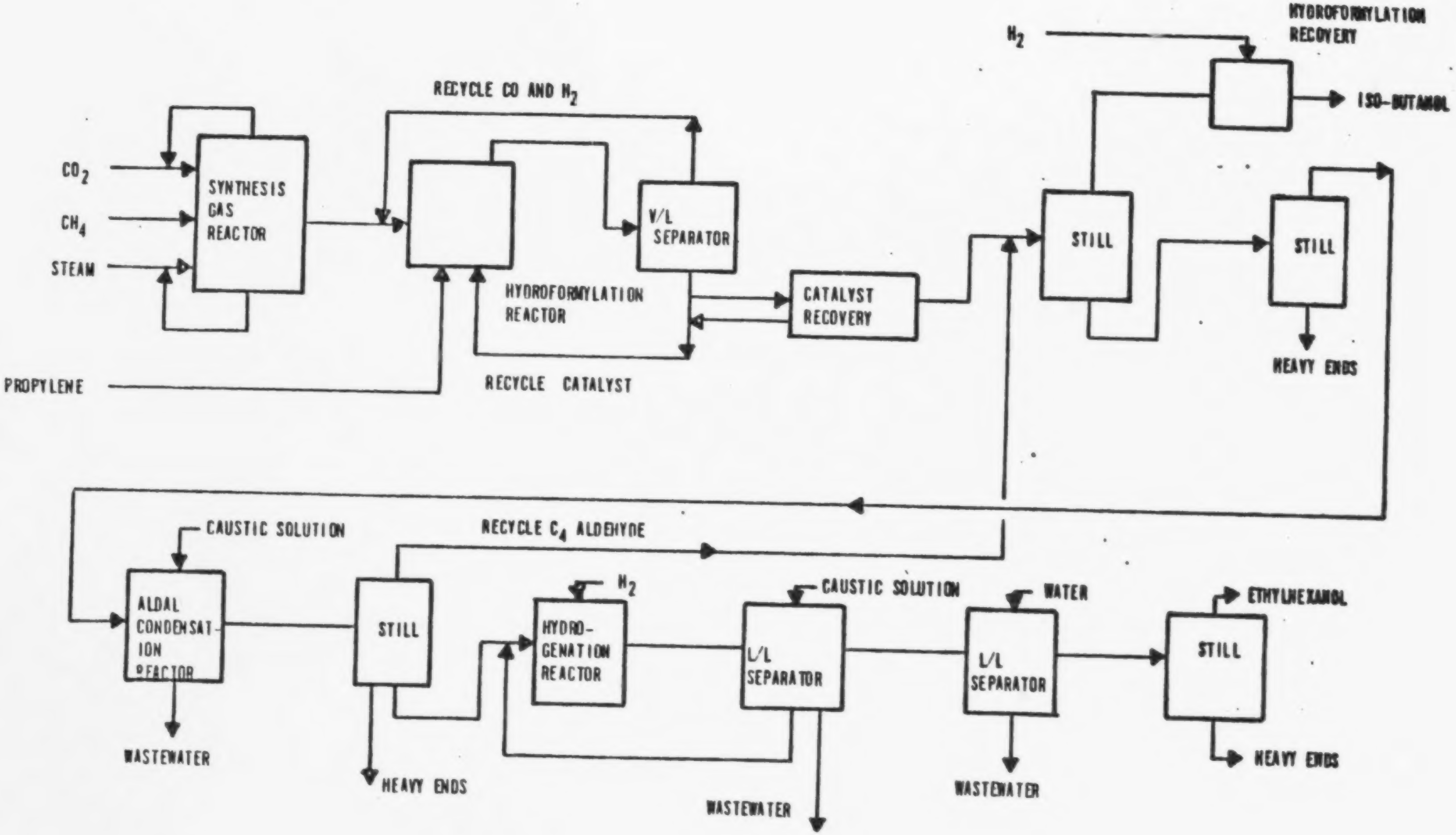
Other products made are iso-butyraldehyde and n-butyraldehyde.

○ gaseous emissions

△ liquid emissions

☐ solid emissions

FIGURE 5-4. MANUFACTURE OF 2-ETHYL HEXANOL BY CARBONYLATION.



Source: USEPA, 1974.

Fugitive emissions will occur from every piece of equipment.

the chemicals, and efficiency, age, and maintenance of the equipment. However, the major environmental concern for a carbonylation process will be the off-gas vented from the reactor and the disposal of the heavy residues. Because gaseous carbon monoxide is an odorless and colorless gas, an efficient detection system is required to detect it. Versar contacted both Monsanto and Borden, Inc. and found that personal detectors and air monitors are used in the plants to detect carbon monoxide leaks. Further information was considered proprietary.

REFERENCES

Hedley, W.H., S. M. Mehta, C. M. Moscowitz, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Co.

Herrick, E.C., J. A. King, R. P. Oullette. 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Kirk, Othmer. 1978. Encyclopedia of Chemical Technology (Volumes 1 & 4). New York, New York: John Wiley & Sons.

Shreve, N. 1967. Chemical Processes Industries, 3rd ed. New York, New York: McGraw Hill Book Company.

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

USEPA. 1974. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemical Manufacturing. Point Source Category. Washington, DC: U.S. Environmental Protection Agency.

USEPA. 1980. U. S. Environmental Protection Agency. Organic Chemical Manufacturing, Volume 10: Selected Processes. Research Triangle Park, NC: USEPA, Office of Air Quality.

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SECTION 6

CONDENSATION

6.0 INTRODUCTION

Condensation is the process where two or more organic chemicals combine to form a main product, usually with the separation of water or some other low-molecular-weight compound (Herrick 1979). Very diverse groups of organic chemicals are made from condensation reactions. For instance, some pesticides are made by halogenation followed by condensation. Table 6-1 lists the 55 organic chemicals manufactured by condensation (Herrick 1979) and figures for their production in 1980 (SRI 1981). Many other processes are required in addition to the condensation process to make these chemicals.

Within the condensation manufacturing process train, we can generalize the process steps required. Although process sequences may vary from chemical to chemical, generally they are: 1) preheating the reactants, 2) condensation reactor, 3) cooling the products, 4) purifying the products, and 5) separating the products. Not all reactions will require heating and cooling; gaseous, liquid, and slurry reactions are possible.

Condensation reactors may be be packed columns, furnaces, agitated tanks. or fluidized columns. Purification of the products is necessary to remove impurities such as catalysts, unreacted reactants, and the low-molecular weight end-products. This step may have centrifuges, degassers, and caustic and water scrubbers. The products will have to be further separated from solvents, excess reactants, and by-products by conventional or extractive distillation or strippers. Any combination of equipment and flows is possible. Figure 6-1 shows a generalized flow diagram for a condensation process.

TABLE 6-1. CONDENSATION PRODUCTS AND THEIR MANUFACTURE IN 1980

Product	Amount[1,2] kkg	Feedstock	Other Required Processes
Acetic anhydride	726,000[1]	Acetic acid	Pyrolysis
Arsanilic acid (p-aminobenzenearsonic acid)	NA[3]	Aniline Arsenic acid	None
Benzene sulfonyl chloride	NA[3]	Benzene Chlorosulfonic acid	None
Biphenyl (diphenyl)	26,400[2]	Benzene	Dehydrogenation
Bisphenol A	330,200[1]	Acetone Phenol	None
Choline chloride	NA[3]	Ethylene oxide Trimethylamine	Amination by ammonolysis Hydrohalogenation
Crotonaldehyde n-Butyl alcohol n-Butyraldehyde	NA[3]	Acetaldehyde	Hydrogenation
Dichlorodiphenyl-trichloroethane [1,1,1-trichloro-2,2-bis-(p-chlorophenyl) ethane](DDT)	26,800[4]	Acetaldehyde Monochlorobenzene	Halogenation
2,4-Dichlorophenoxyacetic-acid (2,4-D)	5,800[2]	Monochloroacetic acid Phenol	Halogenation
2-(2,4-Dichlorophenoxy) propionic acid (2,4-DP)	NA[3]	α-Chloropropionic acid 2,4-Dichlorophenol	Dehydrohalogenation
4,4'-Dichlorophenylsulfone	NA	Monochlorobenzene Sulfur trioxide	None
Diphenylamine	NA[3]	Aniline	None
Diphenylguanidine	NA[3]	Aniline	None
N,N'-Diphenylhydrazine (hydrazobenzene)	NA[3]	Cyanic acid Nitrobenzene	Hydrogenation
Diphenylmethane-4-4'-diisocyanate [(methylene-bis(4-phenylisocyanate)] (MDI)	209,000[1]	Aniline Formaldehyde Phosgene	Phosgenation

TABLE 6-1. CONDENSATION PRODUCTS AND THEIR MANUFACTURE IN 1980 (continued)

Product	Amount[1,2] kkg	Feedstock	Other Required Processes
Ethyl acetate	94,300[1]	Acetaldehyde	None
Ethyl carbonate	NA[3]	Ethylene oxide Carbon dioxide	None
Ethylene glycol ethers	555,000[5]	Alkyl alcohols Ethylene glycol	None
Ethylene glycol monoethyl ether		Ethylene oxide Ethanol	None
Ethyl ether (diethyl ether)	23,200[1]	Ethanol	None
2-Ethylhexanol	125,200[1]	Acetaldehyde Butyraldehyde	Hydrogenation
Ethyl parathion (parathion)	NA[3]	0,0-Dimethyl phosphoro-Thionochloridate Sodium nitrophenoxide	Halogenation
Formic acid	27,200[1]	Carbon monoxide (methanol recycled)	Carbonylation Hydrolysis
Heptenes	54,400[1]	Butylenes Propylene	None
Hexamethylenetetramine	54,000[1]	Ammonia Formaldehyde	Amination by ammonolysis
Isophorone	NA[3]	Acetone	None
Isoprene (2-methyl-1,3-butadiene)	143,300[1]	Propylene	Cracking
Isoprene		Acetone Acetylene	Dehydration Hydrogenation
Isoprene		Formaldehyde Isobutylene	Cracking
Isoprene		Formaldehyde Hydrogen chloride Isobutylene	Hydrohalogenation Pyrolysis

TABLE 6-1. CONDENSATION PRODUCTS AND THEIR MANUFACTURE IN 1980 (continued)

Product	Amount[1,2] kkg	Feedstock	Other Required Processes
N-isopropyl-N'-phenyl-p-phenylenediamine	NA[3]	Acetone Aniline p-Chloronitrobenzene	Alkylation Dehydrohalogenation Hydrogenation
Melamine	54,400[1]	Dicyandiamide	Pyrolysis
Melamine		Urea	Pyrolysis
Mesityl oxide	NA[3]	Acetone	Dehydration
DL-methionine	NA[3]	Acrolein Cyanic acid Methyl mercaptan	Hydrogenation
2-Methyl-2-butanol (tert-amyl alcohol)	NA[3]	Acetone Acetylene	Hydrogenation
2-Methyl-3-butyn-2-ol	NA[3]	Acetone Acetylene	None
2-Methyl-4-chlorophenoxy-acetic acid (MCPA)	NA[3]	o-Cresol Monochloroacetic acid	Halogenation
2-(2-Methyl-4-chlorophenoxy) propionic acid (MCPP)	NA[3]	α-Chloropropionic acid	Dehydrohalogention
2-Methyl-5-ethylpyridine (MEP) (5-ethyl-2-picoline)	NA[3]	Acetaldehyde Ammonia	Amination by ammonolysis
Methyl isobutyl ketone	83,800[1]	Acetone Hydrogen	Dehydration Hydrogenation
Methyl parathion (0,0-dimethyl 0-p-nitrophenyl phosphorothioate)	23,200[4]	0,0-Aimethyl phosthionochloridate Sodium p-nitrophenoxide	Halogenation
4-Methyl-1-pentene	NA[3]	Propylene	None
N-phenyl-2-naphthylamine	NA[3]	Aniline 2-naphthol	None

TABLE 6-1. CONDENSATION PRODUCTS AND THEIR MANUFACTURE IN 1980 (continued)

Product	Amount[1,2] kkg	Feedstock	Other Required Processes
Oxalic acid	NA[3]	Sodium formate	Pyrolysis
Pentaerythritol	64,600[1]	Acetaldehyde Formaldehyde	Cannizzaro reaction
p-Phenylphenol (4-hydroxydiphenyl)	NA[3]	Benzene Cyclohexanone	Dehydrogenation
Polyethylene terephthalate	435,400[1]	Dimethyl terephthalate Ethylene glycol	Polymerization
beta-Propiolactone	NA	Formaldehyde Ketone	None
Propylene carbonate	NA[3]	Carbon dioxide Propylene oxide	None
Pyridine beta-Picoline	21,800[1]	Acetaldehyde Formaldehyde Methanol	Ammoxidation
Tetrahydrofuran, 2,3,4,5-tetracarboxylic dianhydride	57,300[1]	Furan Maleic anhydride	Oxidation
Tetramethylthiuram disulfide (thiram) [bis(dimethylthiocarbamoyl)-disulfide]	NA[3]	Ammonia Carbon disulfide Dimethylamine Hydrogen peroxide	Oxidation
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	6,600[4]	Acetic acid 2,4,5-Trichlorophenol	Halogenation
Zineb (zinc ethylenebisdithiocarbamate)	800[2]	Carbon disulfide Ethylene diamine Zinc sulfate	None

TABLE 6-1. CONDENSATION PRODUCTS AND THEIR MANUFACTURE IN 1980 (continued)

Product	Amount[1,2] kkg	Feedstock	Other Required Processes
Ziram (zinc dimethyldithio-carbamate)	1,700[2]	Carbon disulfide Dimethylamine Zinc sulfate	None

Source: Herrick 1979.

[1] Source: SRI 1981. Assume 80% of capacity is produced and also assume that the amount produced was by condensation.

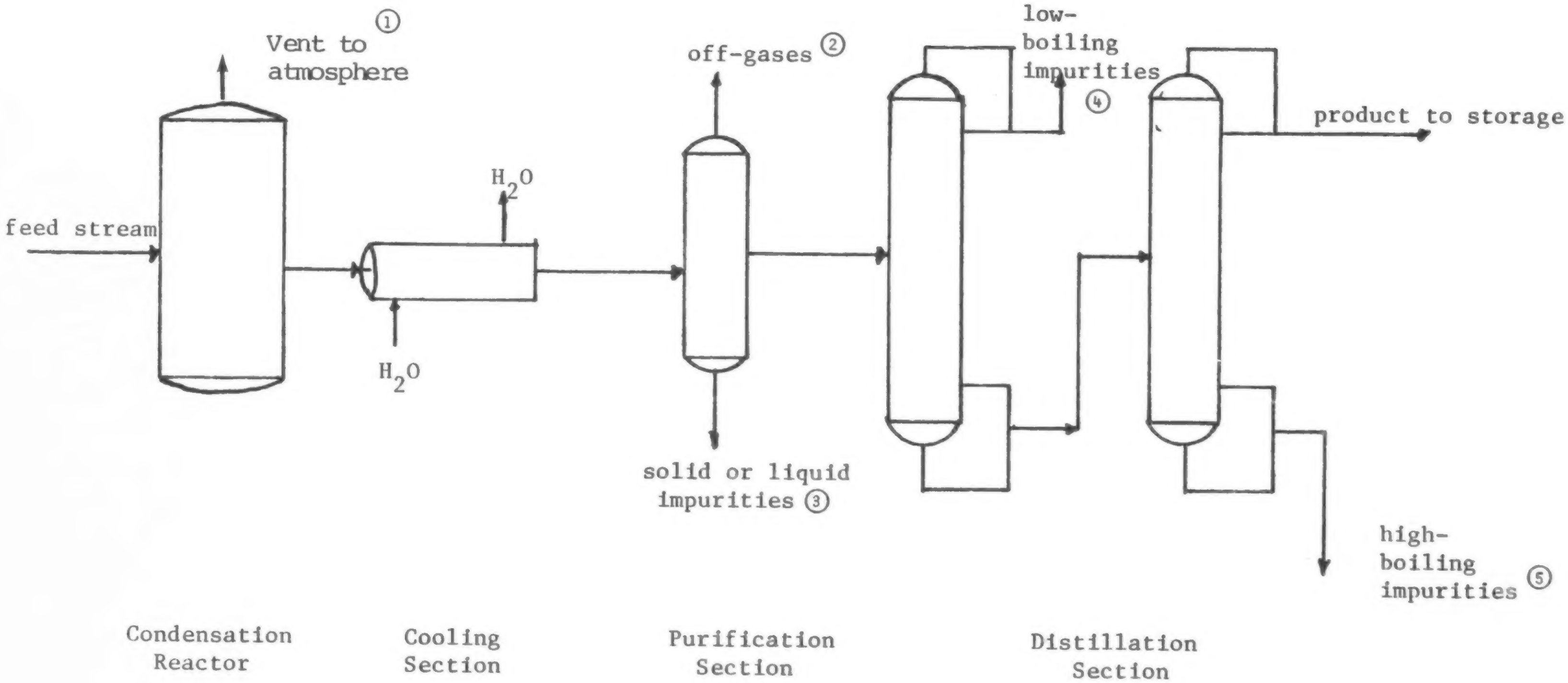
[2] Source: USITC 1979.

[3] Source: SRI 1981. Does not give amounts produced, but lists producers.

[4] Source: USITC 1975.

[5] Source: USEPA 1980. Most of the 555,000 kkg were produced by a different reaction - the reaction of ethylene oxide and alcohols.

Figure 6-1 A Generalized Flow Diagram of a Condensation Process



Nomenclature

O Location of Emission Points

6.1 GENERAL CHEMISTRY

A condensation reaction occurs when two chemicals combine to form a main product with an additional end-product of a small molecule such as water. For example, acetic anhydride is formed from a two-step condensation reaction using acetic acid and ketene. In the first step, acetic acid is dehydrated to form ketene and water. The second step is the reaction of ketene and acetic acid to produce acetic anhydride. The following paragraphs describe the particulars of each step of the condensation reaction to make acetic anhydride.

The first reaction is the endothermic decomposition of acetic acid to ketene and water, as shown in reaction (1).

$$\underset{\textbf{(acetic acid)}}{\mathbf{CH_3COOH}} \xrightarrow[\substack{AlPO_4 \\ 0.13\text{-}0.26\ \text{atm}}]{700\text{-}720^{\circ}C} \underset{\textbf{(ketene)}}{\mathbf{CH_2{=}C{=}O}} + \underset{\textbf{(water)}}{\mathbf{H_2O}} \tag{1}$$

This reaction occurs at 700-720°C under reduced pressure in a pyrolysis furnace. The dehydration catalysts are aluminum phosphate and triethyl phosphate. Many decomposition reactions are competing with reaction (1). The reaction by-products, carbon, carbon dioxide, carbon monoxide, methane, hydrogen, and ethylene, may be formed by any of the following reactions:

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{exothermic} \tag{2}$$

$$CH_3COOH \rightarrow 2\,CO + 2\,H_2 \qquad \text{endothermic} \tag{3}$$

$$2\,CH_2{=}C{=}O \rightarrow CH_4 + C + 2\,CO \qquad \text{exothermic} \tag{4}$$

$$2\,CH_2{=}C{=}O \rightarrow C_2H_4 + 2\,CO \qquad \text{exothermic} \tag{5}$$

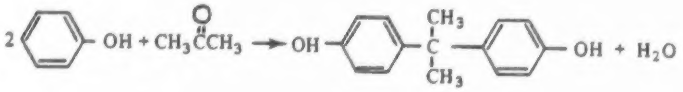
The best conversion gives about 55.2 mole% ketene (Kirk-Othmer 1980). The course of the reaction is very sensitive to temperature, pressure, and contact time to obtain a high ketene yield.

The second step of the condensation reaction to make acetic anhydride is the addition of ketene gas to liquid acetic acid in absorption columns to produce acetic anhydride. The columns are operating under reduced pressures (0.065-0.2 atm) and near-ambient temperatures (30-40°C).

$$\underset{\text{(acetic acid)}}{CH_3COOH} \quad + \quad \underset{\text{(ketene)}}{CH_2{=}C{=}O} \quad \longrightarrow \quad \underset{\text{(acetic anhydride)}}{(CH_3CO)_2O} \qquad (6)$$

Because ketene is a very reactive gas, no catalyst is required. Higher temperatures and pressures promote ketene dimerization which is undesirable because diketene is hard to remove from acetic anhydride because of their very close boiling points. Therefore, the temperature and pressure are kept low for the best conversion of ketene and acetic acid to acetic anhydride.

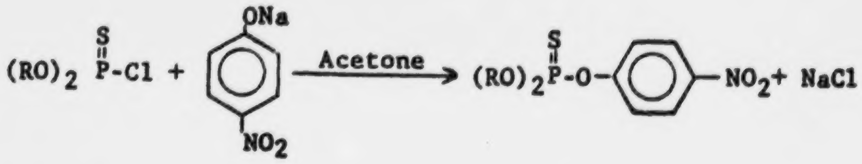
Bisphenol A is another condensation product. It is formed from the condensing of two moles of phenol with one mole of acetone, as shown in reaction (7).



(7)

Dry hydrochloric acid (HCl) is the catalyst for this reaction which occurs at 50°C for 8 to 12 hours.

An example of a condensation reaction where water is not an end-product is the formation of the pesticide, parathion. It is a product of the reaction between O,O-diethyl phosphorothionochloridate and sodium nitrophenoxide, as shown in reaction (8).



(8)

The small additional end-product from this reaction is sodium chloride.

All of the condensation reactions are very different. Different catalysts, temperatures, pressures, and reacting vessels are employed for every condensation chemical. A variety of organic chemicals are included under condensation reactions. Basically, it is the catch-all for chemicals that do not fall under another reaction class, such as alkylation or sulfonation. By definition, it is the reaction of two or more different chemicals to form one main product. An additional, small end-product may be formed but not necessarily.

6.2 DESCRIPTION OF DISCHARGES

Releases from a condensation process will occur as fugitive and particulate gaseous emissions, liquid wastes, and solid residues. The major sources of gaseous emissions are from the reactor by-product vents, the column vents on distillation columns, and releases during storage and handling. Since most condensation reactions yield water as a product of the reaction, a contaminated water stream will be discharged to wastewater treatment. Other liquid emissions will occur from disposal of spent scrubbing liquids and other solvents. Solid residues will result if a by-product of the reaction is a low molecular weight solid (such as salt (NaCl), which is separated from the other products but contaminated to the same degree as the water of reaction. This solid product may be used elsewhere or disposed of. Another source of solid residues is the bottoms product of the heavy ends distillation column.

Volatile organic compounds (VOCs) will be emitted since the condensation products and reactants are organic compounds. Volatile organic compunds (VOCs) have been defined by USEPA as organic compounds which, when emitted to the atmosphere, undergo photochemical reactions producing ozone. Most every organic chemical is a volatile organic compound (VOC). Also included as condensation products are pesticides. The emissions during their manufacture should be carefully monitored and controlled when possible.

Fugitive emissions - may occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains, and cooling towers.

Preheating the reactants - if steam evaporators or heat exchangers are used, the steam will become contaminated.

Furnaces - the combustion gases will be contaminated with incomplete combustion product and oxides of nitrogen (NO_x).

- hydrocarbon and coke particulate emissions will occur when decoking the furnace.

Reactors - fugitive emissions will occur from reactors when the catalysts or packing are regenerated; this will create an intermittent gaseous or liquid waste stream.

Product cooling - quench waters or solvents will become contaminated because they come in direct contact with the products.

- cooling waters may become contaminated through leaks in the heat exchangers.

Product purification - when centrifuges are used, absorbers and caustic and water scrubbers will have contaminated liquid waste streams.

- gas scrubbers generally vent or flare pollutants to the air.

Product separation - if conventional or extractive distillation is used, fugitive emissions will occur, and the unwanted heavy bottoms product will have to be disposed of or reused.

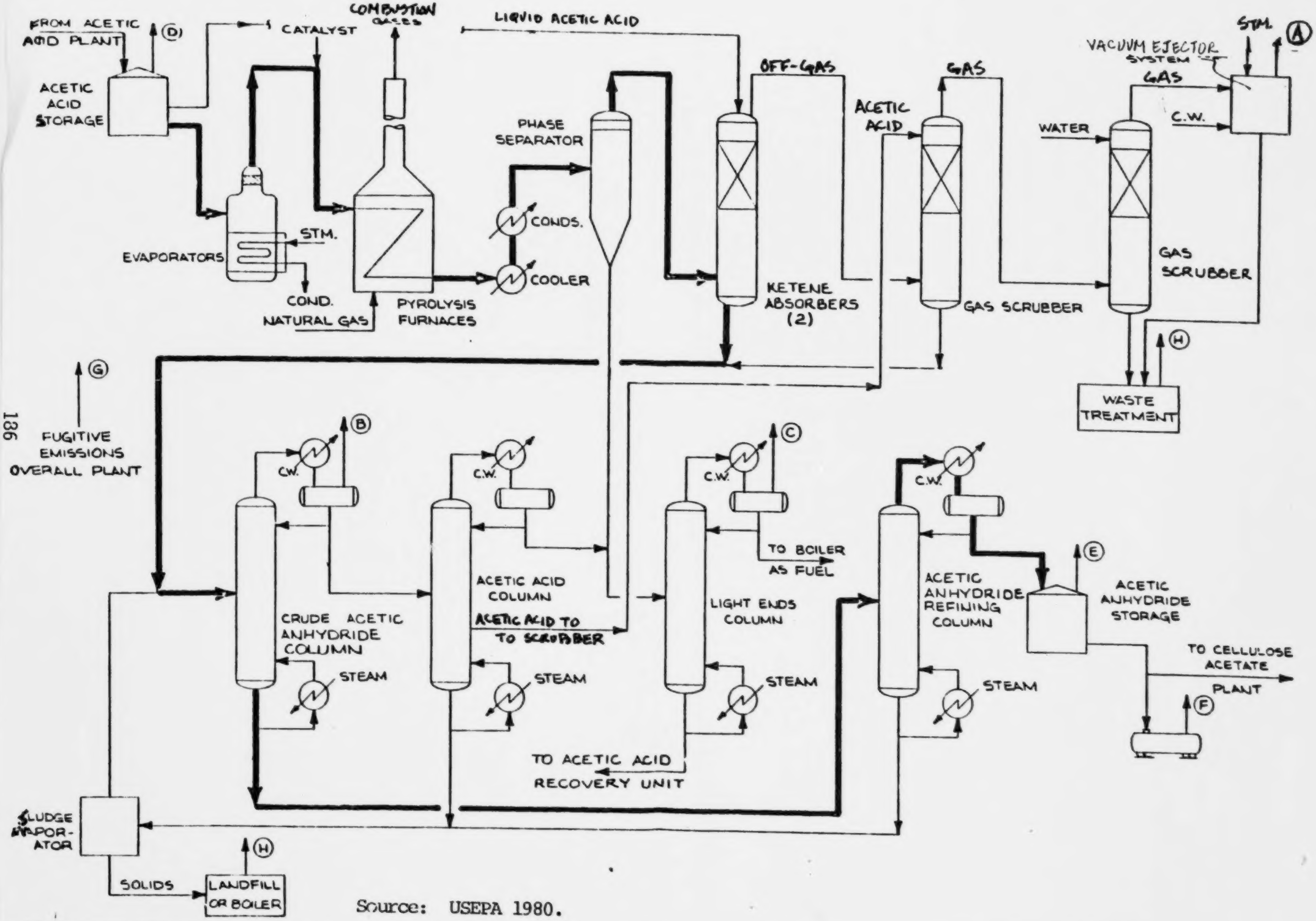
Stream generation & cooling tower operation - contaminants are released during operation and at blowdown.

6.3 PRODUCTION PROCESS - ACETIC ANHYDRIDE PRODUCTION

The condensation chemical with the largest production volume is acetic anhydride. It is a product of two successive condensation reactions: the endothermic decomposition of acetic acid to ketene (gas phase) and the subsequent addition of acetic acid to ketene to make acetic anhydride (liquid phase). As discussed in Section 6.1, acetic acid can decompose to many products; therefore, the temperature, pressure, and contact time must be carefully monitored to optimize the conversion of acetic acid to acetic anhydride, which is a colorless liquid with a penetrating, choking odor. The chief impurity in acetic anhydride is acetic acid (Kirk-Othmer 1980). (This process description section was written from information gathered from Hedley (1975), Kirk-Othmer (1980), and USEPA (1980).)

Figure 6-2 is a detailed flow diagram for the production of acetic anhydride from acetic acid. Briefly, the process sequence is as follows. First, the acetic acid is preheated and sent to a pyrolysis furnace where it undergoes a catalytic decomposition to form ketene and water. The gaseous decomposition products are cooled and sent to a condenser. The water and unreacted acetic acid are condensed in the condenser and separated from the ketene gas in a vapor-liquid separator. The ketene and reaction by-product gas pass to absorption columns where the ketene is contacted with liquid acetic acid to form liquid acetic anhydride. The absorption columns have vents that pull off unreacted gases which proceed to gas scrubbers to be neutralized and separated. The crude, liquid acetic anhydride passes to the distillation section to be separated from the high- and low-boilng impurities. The first distillation column removes the low-boiling impurities, which are mostly acetic acid and any dissolved, unreacted gases. These low-boiling impurities are further separated in two small distillation columns to obtain pure acetic acid. The second acetic anhydride distillation column removes the high-boiling impurities which consist of water and propionic acid. The acetic anhydride product is sent to product storage, and the high-boiling impurities are sent to sludge

FIGURE 6-2. FLOW DIAGRAM FOR UNCONTROLLED ACETIC ANHYDRIDE MODEL PROCESS.



Source: USEPA 1980.

evaporators. The residue from the evaporators is landfilled or used as boiler fuel. In the following process description, the emission points from each process step are indicated, and the emissions are quantified where information was available.

6.3.1 Pyrolysis Furnace

The pyrolysis furnace section includes vaporization of liquid acetic acid in steam evaporators and the dehydration reaction of acetic acid to ketene and water in a pyrolysis furnace. First, liquid acetic acid is fed from storage to steam evaporators where it is vaporized. The gaseous acetic acid is then combined with dehydration catalysts, such as aluminum phosphate or triethyl phosphate, before entering the pyrolysis furnace. This feed stream is fed under vacuum to the pyrolysis furnace where it undergoes an endothermic decomposition to form ketene gas and water vapor. Other gaseous by-products are formed such as carbon dioxide and carbon monoxide, methane, hydrogen, and ethylene. Lower yields of ketene mean higher amounts of gaseous by-products. The yield of ketene is very sensitive to the temperature, pressure, and reaction time. The pyrolysis furnace is externally fired to a temperature of 700 to 720°C by natural gas and is operated under a reduced pressure of 0.13-0.26 atmospheres. The reaction tubes must be made of a high-chromium steel and be free of nickel in order to be resistant to high temperatures, acid vapors, and oxidizing conditions. Coke deposits easily form on these reaction tubes and must be removed periodically by passing hot steam through them. Ammonia is added at the furnace exit to neutralize the catalysts and stabilize the ketene gas, which is very reactive. All products, including the catalysts, pass out of the pyrolysis furnace and proceed to the separators to separate out the water of this reaction before the ketene gas is used in the succeeding condensation reaction.

6.3.1.1 Emissions from Pyrolysis Furnace

The steam used in the steam evaporator does not come into direct contact with the acetic acid it is heating; however, the steam may become contaminated with acetic acid as the result of leaks in the evaporator.

The combustion gases from the gas-fired pyrolysis furnace may be fairly high in oxides of nitrogen (NO_x) content because of high-flame temperature and non-stoichiometric combustion control (Radian 1977). Sulfur emissions are low because most furnaces burn sulfur-free, plant-produced fuel. Hydrocarbon and coke particulate emissions to the atmosphere occur when the furnaces are decoked.

Hydrocarbon and coke particulate emissions to the atmosphere will occur when the furnace tubes are regenerated with steam. The tubes are regenerated four to six times a year during plant shutdown (USEPA 1980). Fugitive emissions from the pyrolysis furnace will be minimal since it is under reduced pressure. The pressure will be monitored and major leaks will be detected and rapidly fixed.

6.3.2 Cooling, Condensing, and Phase Separation

The water formed from the dehydration reaction, the unreacted acetic acid, and the ammonia metophosphate catalysts must be removed from the products exiting the pyrolysis furnace before the ketene gas can further be reacted with acetic acid to form acetic anhydride. These by-products of the first reaction are removed by condensing them and separating them out in the liquid phase from the ketene gas. First, the gaseous stream exiting the pyrolysis furnace is cooled in heat exchangers from 700°C to almost 100°C. Then the stream passes through condensers which condense the water, unreacted acetic acid, and ammonium metophosphate catalysts. The two-phase stream is separated in a vapor-liquid separator. The vapor fraction consisting of the uncondensed ketene gas and gaseous by-products proceeds to the ketene absorbers to be further reacted. The liquid fraction of water, unreacted acetic acid and ammonia metophosphate catalysts is sent to the acetic acid column in the distillation section to be separated.

A process variation used by one-half of the companies producing acetic anhydride is to quench the exiting pyrolysis gases with benzene, instead of cooling, condensing, and separating. When the gaseous products are quenched, the water, unreacted acetic acid, and catalysts condense and leave the bottom of the quench tower with the benzene. This liquid fraction is further separated in an additional distillation column to recover the benzene for reuse. The uncondensed gases exit from the top of the quench tower and proceed to the ketene absorbers.

6.3.2.1 Emissions from Cooling, Condensing, and Phase Separation

The cooling water in the heat exchangers and condensers may become contaminated from leaks within the heat exchangers and condensers. Fugitive emissions from vapor-liquid separators may occur as the result of leaks in the separator.

The emissions from the benzene-quench variation will occur as fugitive emissions at fittings, valves, pumps, etc., from the quench tower. Some benzene will vaporize and be carried with the gas stream to the ketene absorber.

6.3.3 Ketene Absorbers

The second step of the condensation reaction to produce acetic anhydride takes place in ketene absorbers. The ketene gas from the phase separator, which consists of ketene, carbon oxides, methane, hydrogen, and ethylene, is contacted with liquid acetic acid in two absorption columns operating in series. When the ketene gas proceeding up the column is contacted with the liquid acetic acid coming down the column, liquid acetic anhydride is formed and falls to the bottom of the column. These packed columns are operated at near ambient temperatures (30-40°C) and under reduced pressure (0.065-0.2 atm). No catalyst is required. The crude acetic anhydride product, containing 10% acetic acid, proceeds to the distillation section for purification. The unreacted gases which proceed up the absorption columns exit through absorber off-gas vents at the top of the columns. These gases, which also contain reaction by-product gases of acetic acid, acetic anhydride, and ketene, are sent to gas scrubbers for the removal of acetic acid and acetic anhydride.

6.3.3.1 Emissions from Ketene Absorbers

Fugitive emissions may occur from the ketene absorbers at the valves, seals, and pumps. These emissions are expected to be minor since the columns are operating under reduced pressure. A major leak will be easiy detected and rapidly fixed. The packing in the ketene absorbers may be regenerated with steam during plant shutdown. This will cause an intermittent gaseous waste stream containing hydrocarbons.

6.3.4 Gas Scrubbers

Reaction by-product gases from the absorber off-gas vent are sent to gas scrubbers to remove the acetic acid and acetic anhydride before venting these gases to the atmosphere. The reaction by-product gases contain carbon dioxide, carbon monoxide, acetic acid, acetic anhydride, methane, hydrogen, ethylene, and traces of ketene. Two scrubbing columns are used. The first scrubbing column uses a strong acetic acid solution. As the gases proceed up the column, they are contacted with the acetic acid solution. The solution absorbs the acetic acid and acetic anhydride gases out of the gas mixture and exits at the bottom of the column. The spent acetic acid solution is sent to the crude acetic anhydride distillation column. The gases from the first scrubber proceed to the second scrubber which uses water as its scrubbing solution. The gases are contacted with the water as they proceed up the column. The spent water from this scrubber is discharged to the sewer for wastewater treatment. The gases exiting from the second scrubber pass through the vacuum system, which provides the required reduced pressure for the process, and exit from a vent to the atmosphere. Most acetic anhydride manufacurers route these gases to the pyrolysis furnace to be used as fuel (thermal oxidation). Table 6-2 shows the composition of this exiting gas mixture from a typical acetic anhydride plant (USEPA 1980).

6.3.4.1 Emissions from Gas Scrubbers

Fugitive emissions will occur from the gas scrubbers. The packing in the scrubbing columns may be regenerated; this will cause an

TABLE 6-2. COMPOSITION OF REACTOR BY-PRODUCT GAS[a]

Component	Composition (wt %)	Emission Ratio (kg/kkg[b])
VOC		
Propane	4	0.73
Ethylene	8	1.5
Propadiene	10	1.9
Other VOC[c]	2	0.37
Total VOC	24	4.50
Other Components		
Methane	5	0.95
Carbon monoxide	37	7.0
Carbon dioxide	27	5.0
Others[d]	7	1.3
Total	100	18.75

Source: USEPA 1980.

[a] Model acetic anhydride plant: 110 x 10^6 kkg/yr plant.
8760 hours/year in operation.

[b] Kg/kkg of acetic anhydride.

[c] Includes hydrocarbons such as propylene, butylene, and butadiene.

[d] Includes nitrogen, oxygen, and water.

intermittent emission of hydrocarbons. The spent scrubbing water will be contaminated with hydrocarbons and sent to wastewater treatment. This concentration of hydrocarbons in the spent water will be the solubility of the hydrocarbon in water.

The largest process emission is the reaction by-product gas emitted from the vacuum system after it has been processed through the gas scrubbers. This emission has been estimated to be 56.5 kg/hr for a 110 Gg/yr model plant containing 37% carbon monoxide, 27% carbon dioxide, and 36% hydrocarbons, by weight (USEPA 1980) (see Table 6-2). USEPA (1980) reported most acetic anhydride manufacturers use these reaction by-product gases as fuel in the pyrolysis furnace instead of emitting them to the atmosphere.

6.3.5 Distillation for Product Purification

The crude acetic anhydride product contains 10% acetic acid and other impurities (USEPA 1980). It is purified in two atmospheric distillation columns. The first column, called the acetic anhydride column, separates the low-boiling impurities, which are mostly acetic acid, from the acetic anhydride. The low-boiling impurities pass as the overhead product to further distillation to separate out the acetic acid. The bottoms product is the acetic anhydride, and it is sent for further distillation. The second distillation column is called the acetic anhydride refining column which separates the acetic anhydride from the high-boiling impurities. The acetic anhydride product exits as the overhead product and is sent to product storage. The high-boiling impurities are sent to a sludge evaporator to recover any acetic acid or acetic anhydride. The acetic acid or anhydride vapors evaporated off are recycled back to the distillation train. The heavy residue from the evaporator is either landfilled or burned in the pyrolysis furnace.

The low-boiling impurities, the overhead product from the crude acetic anhydride column, mostly contain acetic acid. Two small distillation columns are used to concentrate the acetic acid. The first column, the acetic acid column, removes the high-boiling impurities contained in the acetic acid as the bottoms product and sends them to the sludge evaporator. An acetic acid solution is drawn off from a sidearm on this column and used in the gas scrubbers. The acetic acid is the overhead product and proceeds to the second column, the light ends column. Also fed to the light ends column is the water, unreacted acetic acid, and the ammonium metophosphate catalysts from the phase separator before the ketene absorbers. The light ends column removes the acetic acid as the bottoms product which is sent to an acetic acid recovery unit to be recycled. The water and catalysts are removed in the recovery unit (however, the recovery unit is elsewhere in the plant and is not considered part of this process (USEPA 1980)). The overhead product is sent to the pyrolysis furnace to be used as fuel.

6.3.5.1 Emissions from Distillation for Product Purification

All of the distillation columns have pressure relief vents in the condensing section which emit dissolved gases and uncondensed VOC. USEPA (1980) has determined this rate to be 8.82 kg/hr for their model plant for all four distillation columns. Fugitive emissions may result from seals, valves, and leaks in the distillation train. The heavy residue from the sludge evaporator is either landfilled or used as fuel.

6.4 SUMMARY OF EMISSION DATA

The air emissions for the USEPA (1980) model plant and a plant using the benzene variation are tabulatd in Table 6-3. The benzene variation has larger VOC and benzene emissions than the model process. A substantial amount of benzene evaporates in the quench tower and proceeds through the rest of the process. Benzene is emitted through the reaction by-product vent after the gas scrubbers and through the column vents on the distillation columns. Table 6-4 shows the composition of the reaction

TABLE 6-3. EMISSIONS FROM PRODUCTION OF ACETIC ANHYDRIDE BY CONDENSATION

				Uncontrolled Emissions			Controlled Emissions	
Pollutant	Source (Designation)	Type of Release +	Receiving Medium	Ratio kg/kkg	Rate kg/hr	Form	Control Technology	Ratio kg/kkg
VOC	reactor by-product gas (A)	r	air	4.5^1	56.5^1	gas	thermal oxidation in pyrolysis furnace	0.045^1
	column vents (B,C)	r	air	0.700^1	8.82^1	gas	thermal oxidation in pyrolysis furnace	0.007^1
CO	reactor by-product gas (A)	r	air	7.00^1	88.2^1	gas	thermal oxidation in pyrolysis furnace	0.070^1
	column vents (B,C)	r	air	NA	NA	gas	thermal oxidation in pyrolysis furnace	NA
VOC	reactor by-product gas (A)	r	air	31.0^2	389^2	gas	thermal oxidation in pyrolysis furnace	0.31^2
	column vents (B,C)	r	air	2.13^2	26.82^2	gas	thermal oxidation in pyrolysis furnace	0.21^2
Benzene	reactor by-products (A)	r	air	4.6^2	57.8^2	gas	thermal oxidation in pyrolysis furnace	0.046^2
	column vents	r	air	0.217^2	2.73^2	gas	thermal oxidation in pyrolysis furnace	0.002^2

+ Indicates a release is routine.

Source: USEPA, 1980, Vol. 10, Report 8, p.IV-2, p.V-2, p.V-3..

[1] Model process: 110,000 kkg/yr operating 8760 hours/year

[2] Model process with process variation using benzene quench: 181,000 kkg/yr operating 8760 hours/year.

TABLE 6-4. COMPOSITION OF REACTOR BY-PRODUCT GAS FROM A PLANT USING THE BENZENE VARIATION[a]

Component	Feed to Furnace (wt %)	Feed to Furnace (kg/hr)	Furnace Stack (ppm)
Methane	2.2	8.85	6.9
VOC	29.7	120.5	1.1
Carbon monoxide	35.2	143.0	1.6
Carbon dioxide	26.0	105.8	
Benzene	4.4	17.8	
Sulfur dioxide			0.0
Nitrates (NO_x)			91.5
Others	6.9	27.91	

Source: USEPA 1980.

[a] Plant capacity: 136,000 kkg/yr.

by-product gas exiting from the vacuum jet ejector vents after the gas scrubbers. The control option used is to route these gases to the pyrolysis furnace to be used as fuel. Table 6-5 demonstrates a typical vent analysis for the crude acetic anhydride column from a process using the benzene variation. There is an additional distillation column to separate the benzene and the water. This column has a vent which emits benzene and VOC similar to the other column vents.

Emissions data were not found for all 55 chemicals undergoing condensation. The data that were available are tabulated in Table 6-6. Since condensation processes are so varied, each process should be looked at individually.

TABLE 6-5. TYPICAL VENT ANALYSIS FOR CRUDE ACETIC ANHYDRIDE COLUMN[a]

	Wt. %	Rate (kg/hr)[b]
Acetic acid	2.9	7.4
Benzene	0.1	0.3
Acetone	1.7	4.3
Acetic anhydride	0.3	0.8
Carbon dioxide	7.8	19.8
Water	59.9	152.2
Nitrogen dioxide	0.1	0.3
Nitrogen	0.5	1.3
Air	26.4	67.1

Source: USEPA 1980, Vol. 10, Report 8, p.B-4.

[a] Reported to USEPA by Celanese Corporation in Pampa, Texas. The plant uses the benzene variation and its capacity is 136,000 kkg/yr.

[b] Vent flow rate: 254 kg/hr.

TABLE 6-6. CHARACTERIZATION OF EMISSIONS FROM THE CONDENSATION MANUFACTURING PROCESSES

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Acetic anhydride	methane	gas scrubber	feed	r	air	NA[1]	NA	gas	NA	NA
	ethylene	vent	feed	r	air	NA[1]	NA	gas	NA	NA
	ketene		feed	r	air	NA[1]	NA	gas	NA	NA
	sodium hydroxide	gas scrubber	caustic	r	water	NA[1]	NA	liquid	NA	NA
	sodium acetate		caustic	r	water	NA[1]	NA	liquid	NA	NA
	heavy ends	incinerator	by-products	r	air	NA[1]	NA	air	NA	NA
Bisphenol A	phenol	aqueous waste	by-products	r	water	7.1[1]	NA	liquid	NA	NA
	COD	stream form		r	water	17.1[1]	NA	liquid	NA	NA
	TOC	HCl recovery, crystallizer, and evaporator. H_2O flow = 133.6 gal/ton product		r	water	5.0[1]	NA	liquid	NA	NA
Crotonaldehyde	acetaldehyde	wastewater	feed	r	water	NA[1]	NA	liquid	NA	NA
	acetaldol	discharge	reaction intermed.	r	water	NA[1]	NA	liquid	NA	NA
	crotonaldehyde		product	r	water	NA[1]	NA	liquid	NA	NA
	heavy ends	incinerator	by-product	r	air	NA[1]	NA	gas	NA	NA
Ethyl ether	sodium sulfate	scrubber	caustic	r	water	NA[1]	NA	liquid	NA	NA
	ethanol	scrubber	feed	r	water	NA[1]	NA	liquid	NA	NA
	sodium hydroxide	scrubber	caustic	r	water	NA[1]	NA	liquid	NA	NA
	ethanol	fractionating column	feed	r	water	NA[1]	NA	liquid	NA	NA
2-Ethyl hexanol[3]	butraldehyde	NaOH recovery and H_2O evaporator	feed	r	air	58.5[1]	NA	gas	NA	NA
	light hydrocarbons	light ends stripper	by-products	r	air	11.3[1]	NA	gas	NA	NA
	heavy ends	incinerator	by-products	r	air	NA[1]	NA	gas	NA	NA

TABLE 6-6. CHARACTERIZATION OF EMISSIONS FROM THE CONDENSATION MANUFACTURING PROCESSES
(continued)

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Hexamethylene-tetramine	formaldehyde	drier	feed	r	air	NA^1	NA	gas	NA	NA
	methanol	-	by-product	r	air	NA^1	NA	gas	NA	NA
	ammonia		feed	r	air	NA^1	NA	gas	NA	NA
	formaldehyde	reactor off-gases	feed	r	air	NA^1	NA	gas	NA	NA
	methanol		by-product	r	air	NA^1	NA	gas	NA	NA
	ammonia		feed	r	air	NA^1	NA	gas	NA	NA
	hexamethylenetetramine		product	r	air	NA^1	NA	gas	NA	NA
	formaldehyde	bleed line from centrifuge wash	feed	r	water	NA^1	NA	liquid	NA	NA
	methanol		by-product	r	water	NA^1	NA	liquid	NA	NA
	ammonia		feed	r	water	NA^1	NA	liquid	NA	NA
	hexamethylenetetramine		product	r	water	NA^1	NA	liquid	NA	NA
Methyl isobutyl ketone	acetone	dehydration column	feed	r	water	NA^1	NA	liquid	NA	NA
	diacetone alcohol		intermediate	r	water	NA^1	NA	liquid	NA	NA
Methyl parathion[4]	SO_2	reactor	by-product	r	air	109^2	NA	gas	NA	NA
	hydrogen sulfide		by-product	r	air	58^2	NA	gas	NA	NA
	organo phosphorus compounds and sulfur	chlorinator	by-product	r	air	115^2	NA	gas	NA	NA
	SO_2	sulfur is produced in chlorinator;	incineration of sulfur	r	air	210^2	NA	gas	NA	NA
	HCl	HCl is produced in chlorinator and sent to waste treatment	by-product	r	water	125^2	NA	liquid	NA	NA
	sodium chloride	parathion unit	by-product	r	water	188^2	NA	liquid	NA	NA
	parathion		product	r	water	5^2	NA	liquid	NA	NA
	p-nitrophenol		by-product	r	water	5^2	NA	liquid	NA	NA
	other organic phosphates		by-product	r	water	5^2	NA	liquid	NA	NA

TABLE 6-6. CHARACTERIZATION OF EMISSIONS FROM THE CONDENSATION MANUFACTURING PROCESSES (continued)

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Pentaerythritol	calcium carbonate	precipitator	by-product	r	land	NA[1]	NA	solid	NA	NA
	acetaldehyde	evaporator and	feed	r	air	NA[1]	NA	gas	NA	NA
	formaldehyde	vacuum	feed	r	air	NA[1]	NA	gas	NA	NA
	methanol	crystallizer	by-product	r	air	NA[1]	NA	gas	NA	NA
	ethanol		by-product	r	air	NA[1]	NA	gas	NA	NA
	hydrocarbons	NA	by-product	r	air	15.0[1]	NA	gas	NA	NA
	sodium formate	vacuum crystallizer	by-product	r	water	NA[1]	NA	liquid	NA	NA
	inorganic sodium salts		by-product	r	water	NA[1]	NA	liquid	NA	NA
Polyethylene[5] terephthalate	ethylene glycol	purification	feed	r	land	.47[1]	NA	solid	NA	NA
	polyethylene glycol	column	by-product	r	land	23.1[1]	NA	solid	NA	NA
	sodium hydroxide and sodium bisulfite		solvent	r	land	.085[1]	NA	solid	NA	NA
	ethylene glycol	finishing	feed	r	land	1.9[1]	NA	solid	NA	NA
	polyethylene glycol	column	by-product	r	land	.085[1]	NA	solid	NA	NA
	miscellaneous chemicals		by-product	r	land	.085[1]	NA	solid	NA	NA
Pyridine[6]	phenol	water layer	by-product	r	water/land	.0003[2]	NA	liquid/sludge	NA	NA
	sulfuric acid	stripping still	catalyst	r	water/land	3.0[2]	NA	liquid/sludge	NA	NA
	chlorides	tails	NA	r	water/land	.15[2]	NA	liquid/sludge	NA	NA
	soluble amides		by-product	r	water/land	.004[2]	NA	liquid/sludge	NA	NA
	acetates		by-product	r	water/land	2.5[2]	NA	liquid/sludge	NA	NA
	paraldehyde		feed	r	water/land	30.0[2]	NA	liquid/sludge	NA	NA
	picolines		by-product	r	water/land	2.5[2]	NA	liquid/sludge	NA	NA

TABLE 6-6. CHARACTERIZATION OF EMISSIONS FROM THE CONDENSATION MANUFACTURING PROCESSES
(continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product
Pyridine	picolines	batch still	by-products	r	water	44.0^2	NA	liquid	NA	NA
	methylethyl pyridine			r	fuel	20.0^2	NA	residue	NA	NA

Sources:

[1]Hedley et al. 1975.
[2]Gruber 1975.
[3]Hedlesy et al. 1975. Based on 22,700 kkg/yr capacity.
[4]Hedley et al. 1975. Based on 20,000 kkg/yr capacity.
[5]Hedlesy et al. 1975. Based on 37,700 kkg/yr capacity.
[6]Hedley et al. 1975. Based on 35,000 kkg/yr capacity.

+ Denotes that release is routine (r) or accidental (a).

REFERENCES

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices. Organic Chemicals, Pesticides, and Explosives Industries. Washington, D. C.: U.S. EPA, Office of Solid Waste. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Co., Inc.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Kirk-Othmer. 1978. Encyclopedia of Chemical Technology. Volume I. New York, New York: John Wiley and Sons.

Morrison, R. T. and R. N. Boyd. 1976. Organic Chemistry, 3rd Ed. Boston, Massachusetts: Allyn and Baron, Inc.

Radian Corp. 1977. Industrial Process Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Research Triangle Park, North Carolina: Industrial Environmental Research Lab., U.S. EPA.

Shreve, R. N. 1967. Chemical Process Industries, 3rd Ed. New York, New York: McGraw Hill Book Company.

SRI International. 1981. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

U.S. EPA. 1980. Organic Chemical Manufacturing: Selected Processes. Volume 10. Washington, D. C.: U.S. EPA: Office of Air Quality.

Von Rumker, R., E. W. Lawless, A. F. Meiners, et al. 1975. Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides. Washington, D. C.: U.S. EPA, Office of Pesticide Programs.

Wetherold, R. G., D. D. Rosenbrook, and B. A. Tichenor. 1981. Assessment of Atmospheric Emissions from Petroleum Refining. Research Triangle Park, North Carolina: U.S. EPA.

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SECTION 7

CATALYTIC CRACKING

8.0 INTRODUCTION

Catalytic cracking is the thermal decomposition of an organic compound in the presence of a catalyst and in the absence of air (Herrick 1979). This process is used mainly to create gasoline, C_3-C_4 olefins, and isobutane by selective decomposition of heavy distillates. In the petroleum industry this process is performed at temperatures of ∿ 455 to 540°C and at pressures slightly above atmospheric. The catalyst is usually a specially prepared composite of silica and alumina (Considine 1974).

In a cracking reaction, a hydrocarbon molecule is broken into two or more smaller molecules. Catalytic cracking can also be considered as some of the other major unit processes, i.e., dehydrogenation and dehydrohalogenation which involve cracking of an organic compound in the presence of a catalyst with a loss of a hydrogen atom or a loss of hydrogen and halogen atoms.

Chemicals that are produced by catalytic cracking other than gasoline are listed in Table 7-1. Each chemical has been discussed under the other major unit process where its production process reactions are more clearly defined. A typical flow diagram for the catalytic cracking process is given in Figure 7-1.

7.1 GENERAL CHEMISTRY

The production of isoprene from isobutylene and formaldehyde is an example of catalytic cracking. Isobutylene is condensed with formaldehyde to give 4,4, dimethyl-m-dioxane as the principal product. The dioxane is decomposed in the presence of an acid catalyst to isoprene, formaldehyde, and water. The following equation shows these reactions:

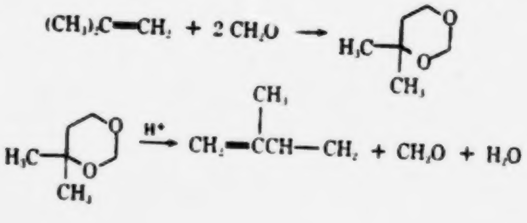


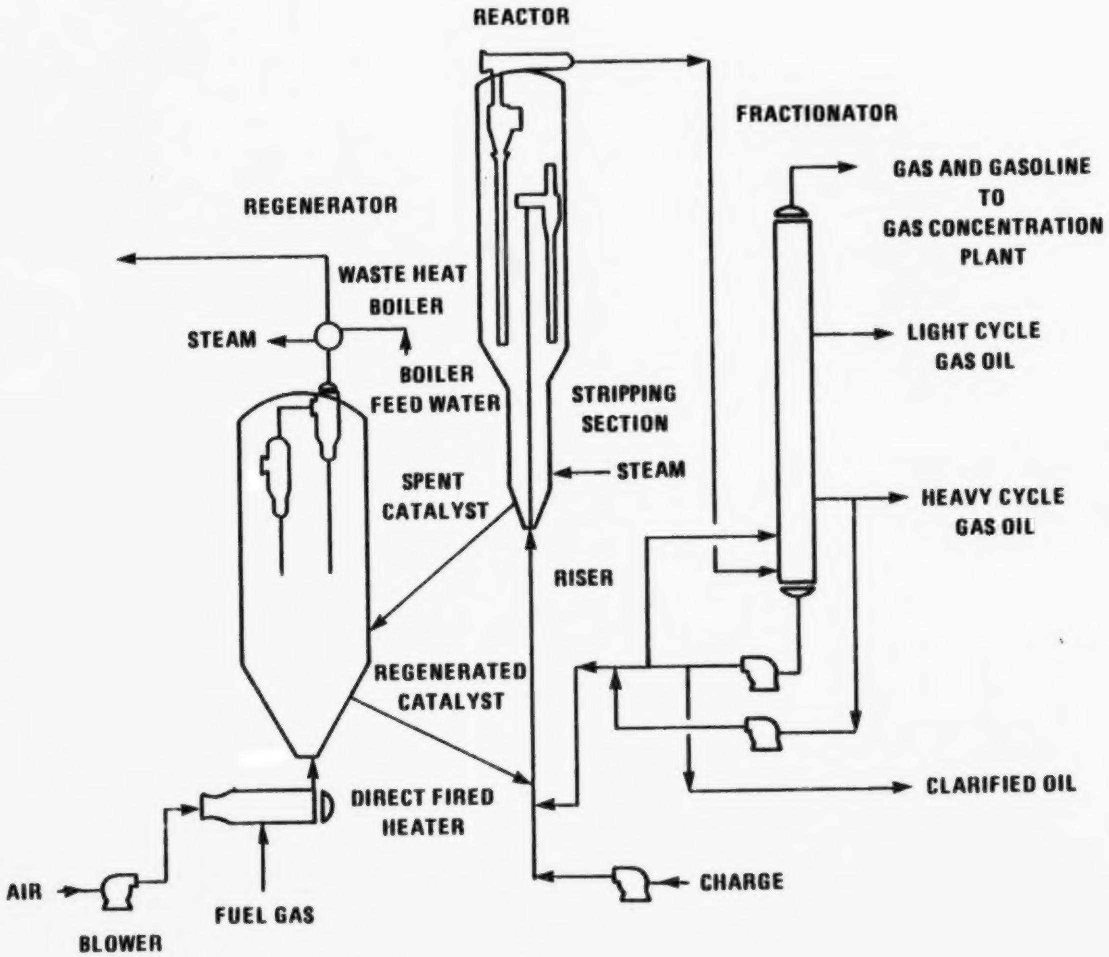
TABLE 7-1. CATALYTIC CRACKING PRODUCTS[1] AND THEIR MANUFACTURE IN 1979[2]

Product	Amount kkg	Feedstock	Other Processes Required
Isoprene	248,561[3]	propylene	condensation
Isoprene	NA	amylenes	none
Isoprene	NA	isobutylene and formaldehyde	condensation
Perchloroethylene and trichloroethylene	NA	ethylene dichloride	halogenation
Perchloroethylene and trichloroethylene	NA	acetylene	halogenation
Perchloroethylene and trichloroethylene	350,640	any C_2 chlorocarbon	halogenation
Vinyl chloride monomer	108,862[4]	acetylene	halogenation
Vinyl chloride monomer	254,012[4]	ethylene	halogenation
Vinyl chloride monomer	NA	naptha	dehydrohalogenation halogenation oxyhalogenation
Vinyl chloride monomer	1,823,440[4]	ethylene	halogenation oxyhalogenation

Sources:

[1] Herrick 1979.
[2] USITC 1979.
[3] Total production from all manufacturing processes.
[4] SRI 1981. Assumed 80% of nameplate capacity.
NA - Not available.

FIGURE 7-1. A TYPICAL FLOW DIAGRAM FOR FLUID CATALYTIC CRACKING



7.2 DESCRIPTION OF DISCHARGES

Releases from a typical catalytic cracking process will result as fugitive emissions from pressure relief valves, vents, seals, and equipment leaks. Catalyst regeneration causes intermittent emission of carbon dioxide, carbon monoxide, and coke and catalyst fines. It is assumed that spent catalyst is landfilled. Other discharges are discussed in the dehydrohalogenation and the dehydrogenation sections.

7.3 PROCESS DESCRIPTION: PRODUCTION OF ISOPRENE FROM PROPYLENE

The process train for isoprene manufacture from propylene is one of the few examples where catalytic cracking is the major required process. Its principal steps are as follows:

1. Propylene is dimerized to 2-methyl-1-pentene.
2. 2-Methyl-1-pentene is isomerized to 2-methyl-2-pentene in the vapor phase over a special silica-alumina catalyst.
3. 2-Methyl-2-pentene is cracked in the presence of hydrogen bromide to form isoprene.

Other compounds that are formed along with isoprene are removed in subsequent distillation steps. Isoprene is purified by superfractionation (Kirk-Othmer 1981).

7.3.1 Emissions from Isoprene Production

Emissions will occur in the cracking section from catalyst regeneration and purging. Other pollutants will be discharged to water from the caustic scrubber and the absorber in the recovery section.

7.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for:

1. Isoprene from propylene (Table 7-2)
2. Vinyl chloride monomer (Table 7-3, Figure 7-2) from ethylene dichloride

Table 7-4 shows the section name and number for other chemicals in Table 7-1 that can be considered to undergo catalytic cracking. Their emissions data has already been presented in these sections.

TABLE 7-2. CHARACTERIZATION OF EMISSIONS FROM THE ISOPRENE FROM PROPYLENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Hydrogen bromide	pyrolysis section	catalyst	r	water	NA	NA	liquid	NA	NA
Isoprene	absorber	product	r	water	1.0	NA	liquid	NA	NA
Heavy ends	recovery column	by-products	r	water	0.2	NA	liquid	NA	NA

Source: Hedley et al. 1975.

+ Emissions are routine (r).

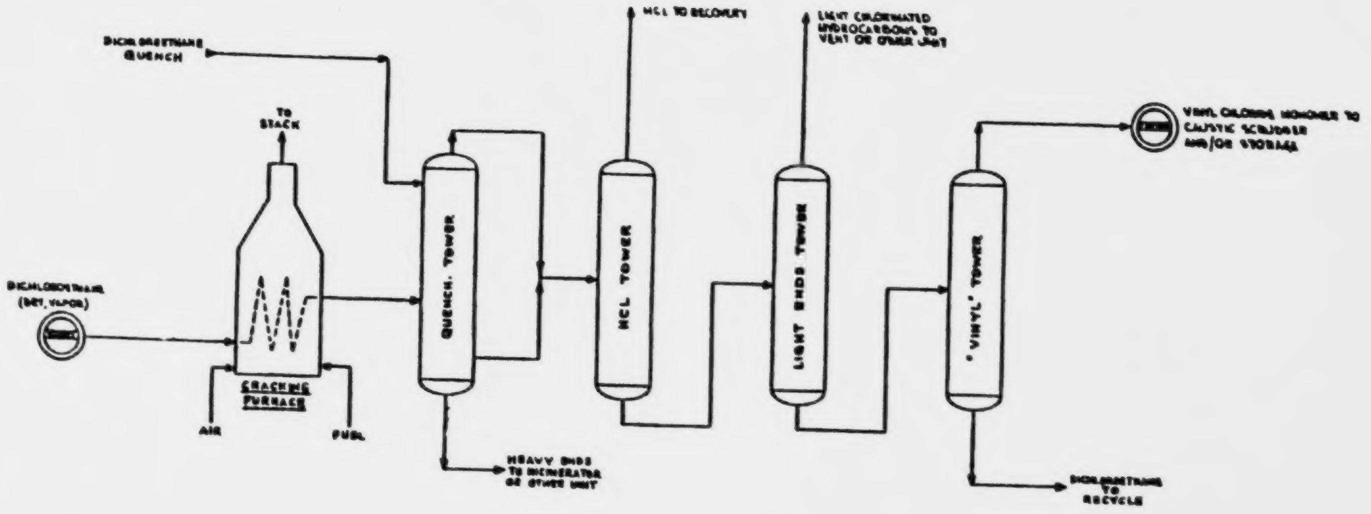
TABLE 7-3. CHARACTERIZATION OF EMISSIONS FROM THE VINYL CHLORIDE MANUFACTURING PROCESS[3]

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Hydrogen chloride	absorber	by-product	r	air	.10[1]	NA	gas	NA	NA
Vinyl chloride		product	r	air	5.0[1]	NA	gas	NA	NA
1,2-Dichloroethylene		by-product	r	air	.15[1]	NA	gas	NA	NA
1,1, Dichloroethylene		by-product	r	air	.40[1]	NA	gas	NA	NA
Acetylene		feed-impurity	r	air	1.5[1]	NA	gas	NA	NA
Ethylene chloride	VCM still	product	r	land	.8[2]	NA	solid	NA	NA
Tars as (C_2HCl)		by-product	r	land	.05[2]	NA	solid	NA	NA
Solids ash		by-product	r	land	.2[2]	NA	solid	NA	NA
Heavy ends		by-product	r	land	37.0[2]	NA	solid	NA	NA

Sources: [1] Hedley et al. 1975. Based on 90,718 kkg/yr capacity.
[2] Gruber 1975.
[3] Feedstock is ethylene dichloride. The EDC is produced from the chlorination of ethylene.

+ Emissions are routine(r).

FIGURE 7-2. MANUFACTURE OF VINYL CHLORIDE BY DEHYDROCHLORINATION OF ETHYLENE DICHLORIDE.


DICHLOROETHANE QUENCH
TO STACK
DICHLOROETHANE (DRY, VAPOR)
CRACKING FURNACE
AIR
FUEL
QUENCH. TOWER
HEAVY ENDS TO INCINERATOR OR OTHER UNIT
HCL TO RECOVERY
HCL TOWER
LIGHT CHLORINATED HYDROCARBONS TO VENT OR OTHER UNIT
LIGHT ENDS TOWER
"VINYL" TOWER
VINYL CHLORIDE MONOMER TO CAUSTIC SCRUBBER AND/OR STORAGE
DICHLOROETHANE TO RECYCLE

Source: Versar 1979.

TABLE 7-4. LOCATIONS OF EMISSIONS DATA

Product	Feedstock	Section Title	No.
Isoprene	amylenes	dehydrogenation	9
Perchloroethylene and trichloroethylene	acetylene	halogenation	12
Vinyl chloride monomer	acetylene	hydrohalogenation	15
Vinyl chloride monomer	ethylene	oxyhalogenation halogenation	19 12

REFERENCES

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Co.

Gruber, G. I. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. For: Office of Solid Waste. Washington, D.C. U.S. Environmental Protection Agency.EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Technomic Publishing.

Herrick, E. C., J. A. King, and R. P. Quellette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science.

Kirk-Othmer. 1981. Encyclopedia of Chemical Technology. 3rd Edition. Vol. 13.

SRI International. 1981 Directory of Chemical Producers - United States. Menlo Park, California.

Versar Inc. 1979. Production and Use of Ethylene Dichloride. For: Office of Water Planning and Standards. Washington, D.C. U.S. Environmental Protection Agency.

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SECTION 8

DEHYDRATION

8.0 INTRODUCTION

The dehydration process involves the production of alkenes from alcohols, by the elimination of a molecule of water.

Dehydration can be carried out in one of two ways:

(1) Heating the alcohol with sulfuric or phosphoric acid to a temperature as high as 200°C.

(2) Passing the alcohol vapor over alumina, Al_2O_3, at 350-400°C, with alumina serving as a Lewis acid (a substance that can take up an electron pair to form a covalent bond, an electron-pair acceptor) (Morrison & Boyd 1973).

Dehydration products, including ethylene, are listed in Table 8-1. Production for 1980 could not be determined from the available literature.

8.1 GENERAL CHEMISTRY

Dehydration is a decomposition reaction. A new compound and water are formed from a single molecule:

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[170^\circ]{95\%\ H_2SO_4} \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

This reaction requires the presence of an acid (catalyst) and the application of heat (Morrison & Boyd 1973).

8.2 DESCRIPTION OF DISCHARGES

Dehydration is part of some major manufacturing processes such as those for urea, isoprene, methyl isobutyl ketone, and mesityl oxide. An extensive literature search and a telephone conversation with E. C. Herrick (September 22, 1981) revealed that dehydration is not used as an independent process in the United States. A process such as ethylene manufacture from ethanol is used in countries with abundant fermentation

TABLE 8-1. DEHYDRATION PRODUCTS

Product	Feedstock	Other Required Processes
Ethylene	Ethyl alcohol	None
Isoprene (2-Methyl-1, 3-butadiene)	Acetone Acetylene	Condensation Hydrogenation
Mesityl oxide (isopropylidene acetone)	Acetone	Condensation
Methyl isobutyl ketone	Acetone Hydrogen	Condensation Hydrogenation
Morpholine	Diethanolamine	None
Urea	Ammonia CO_2	Amination

Source: Herrick et al. 1979.

materials but limited hydrocarbon resources (Kirk-Othmer 1980). Because dehydration is not common as an independent process, no emission data were available.

8.3 PRODUCTION PROCESS: MANUFACTURE OF ETHYLENE BY THE DEHYDRATION OF ETHANOL

The manufacture of ethylene from ethanol is an example of dehydration. The reaction takes place in a fluidized bed reactor where ethanol is contacted with a dehydration catalyst such as alumina, silica-alumina, activated clays, zeolites, etc. The reactor temperature is 370 to 400°C, and the residence time is 1 to 10 seconds.

In Figure 8-1, vaporized ethanol is introduced into a fluidized-bed reactor containing a suitable dehydration catalyst. The gaseous ethanol in the reactor maintains the fluidized state of the catalyst.

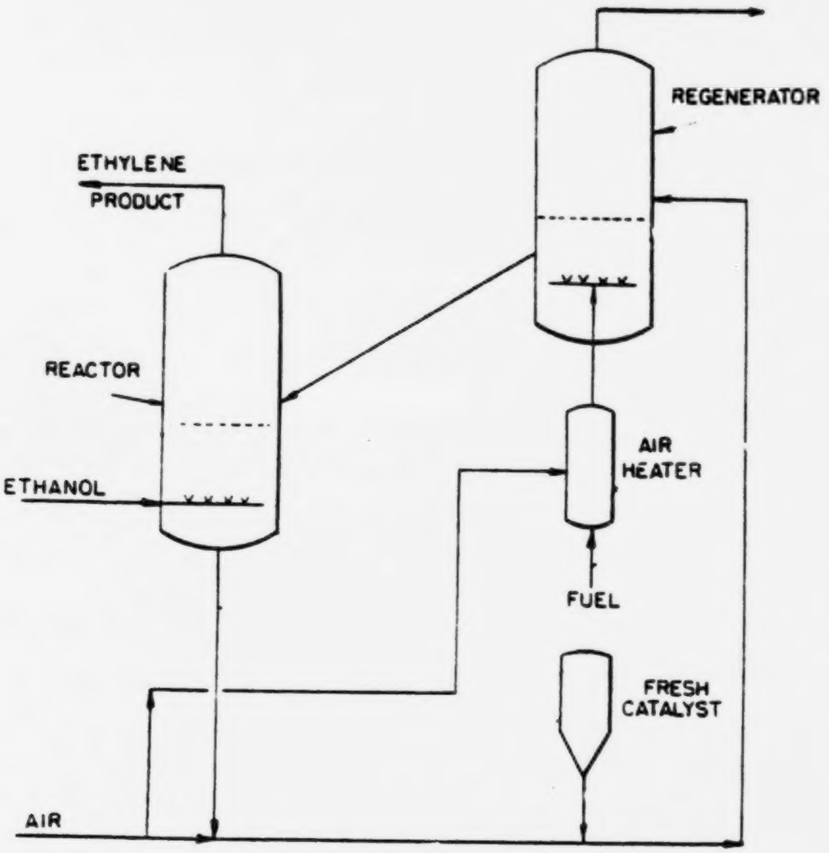
Ethylene product and water, as co-reaction products, exit the reactor and are sent to separation and purification.

The catalyst exits the bottom of the reactor and is transported by air line to a regenerator reactor. Fresh catalyst from a hopper also enters the regenerator through an air line. The catalyst is fluidized in the regenerator by air that first passes through an air heater. Heated catalyst can then be drawn from the regenerator and introduced into the dehydrator reactor. Combustion by-products, as well as air, exit the regenerator reactor (Tsao & Zasloff 1979).

8.4 SUMMARY OF EMISSIONS DATA

No emissions data were available for the dehydration process.

FIGURE 8.1. PROPOSED ETHANOL MANUFACTURING PROCESS BY DEHYDRATION OF ETHANOL



Source: U.S. Patent

REFERENCES

Herrick, E.C., J. A. King, and R. P. Ouellette. 1979. Unit Process Guide to Organic Chemicals Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Kirk-Othmer. 1980. Encyclopedia of Chemical Technology. 3rd Ed. Volume 9. New York: John Wiley and Sons.

Morrison, R. T., and R. N. Boyd. 1973. Organic Chemistry, 3rd Ed. Boston, Massachusetts: Allyn and Bacon, Inc.

Tsao, U., and H. B. Zasloff. Production of Ethylene from Ethanol. U.S. Patent 4,134,926.

REFERENCES REVIEWED BUT NOT CITED

Beauregard, R. E. Process for Preparation of Cis-1,4-Poly(Isoprene). U.S. Patent 4,146,693.

Cook, L. H. Integrated Two-Stage Urea Synthesis. U.S. Patent 4,042,626.

Goetz, N., B. Zeeh, M. Decker, L. Hupfer, H. Toussaint. Manufacture of n-Substituted Tetrahydro-1,4-Oxazines. U.S. Patent 4,068,077.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. For Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, C. M. Moscowitz, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Co.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, N. C. EPA-450/3-80-023.

Young, F. G., L. R. Pennington. Catalytic Process for Dehydration of Alcohols. U.S. Patent 3,780,127.

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SECTION 9

DEHYDROGENATION

9.0 INTRODUCTION

The process of dehydrogenation is a chemical reaction whereby the reactants lose hydrogen. The organic chemical classes concerned are (1) aldehydes and (2) ketones, which are prepared by dehydrogenating alcohols, and (3) olefins, which are prepared from their saturated hydrocarbons. Table 9-1 lists the organic chemicals that are manufactured by dehydrogenation (Herrick 1979). Most dehydrogenation reactions occur over catalysts at high temperatures. The types of dehydrogenation reactors are fixed-bed reactors (packed-bed reactors) and fluidized-bed reactors. Catalyst beds must always be regenerated and purged. After reacting, the products are cooled, purified and separated. A typical dehydrogenation process diagram is presented in Figure 9-1.

The particulars of each dehydrogenation process differ because of different compounds. Some require preparation prior to the dehydrogenation reactor, and others require more involved purification and separation techniques. The preparation techniques are usually one of the 23 processes discussed in other sections of this report; therefore, they are not discussed in this section. The purification and separation processes are discussed in this section, however. Basically, all dehydrogenation processes are the same; they all employ a catalytic bed and a cooling, purification, and separation train.

9.1 GENERAL CHEMISTRY

Dehydrogenation is the process by which a new chemical is formed by the feedstock compound losing a hydrogen. The organic chemicals we are concerned with are aldehydes, ketones, and olefins. Aldehydes and ketones are prepared by dehydrogenating alcohols as shown in reaction 1.

The formation of acetaldehyde from ethyl alcohol is as follows:

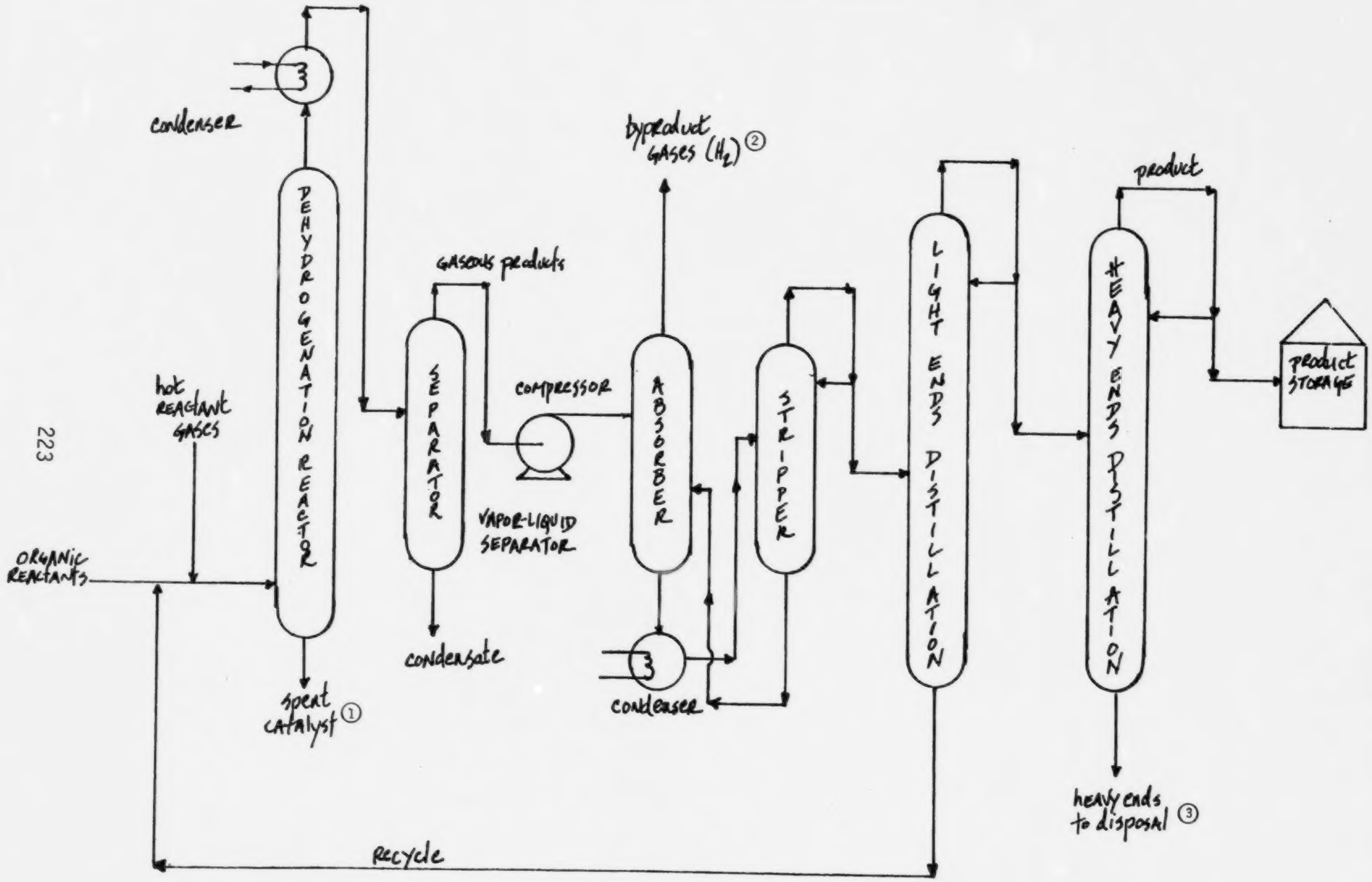
$$CH_3CH_2OH \xrightarrow[250\ -\ 350^\circ C]{Cu\ catalyst} CH_3CHO + H_2(g) \qquad (1)$$

TABLE 9-1. ORGANIC CHEMICALS MANUFACTURED BY DEHYDROGENATION

Product	Amount kkg	Feedstock	Other Required Processes
Acetaldehyde	-	Ethyl alcohol	None
Acetone	-	Isopropyl alcohol	None
Linear alkyl benzenes	102.3	Benzenes Linear paraffin	Alkylation
Biphenyl	26.4	Benzene	Condensation
Butadiene	325.0	*n*-Butane	None
Butadiene		Butene-1 Butene-2	None
Cyclohexanone	396.9	Cyclohexanol/cyclohexane	None
2-Isoamylene	-	Isopentane	None
Isoprene	248.6	Isopentane	None
Isoprene		Tertiary amylenes	None
Methyl ethyl ketone	-	Butene-1 Butene-2	Hydrolysis
Methyl ethyl ketone		sec-Butyl alcohol	None
Phenol	Insignificant amts.	Cyclohexane	Ammoxidation
p-Phenyl phenol	-	Benzene Cyclohexane	Condensation
Piperylene	-	*n*-Pentene	None
Propylene	6440.4	Propane	None
Styrene	3394.8	Benzene Ethylene	Alkylation
Styrene		Ethylbenzene	None
Xylenes, mixed	-	Naphtha	None

Source: Herrick 1979a. SRI, 1979a.

FIGURE 9-1. TYPICAL DEHYDROGENATION PROCESS



Nomenclature

O Emissions Points

Source: Hydrocarbon Processing, 1973.

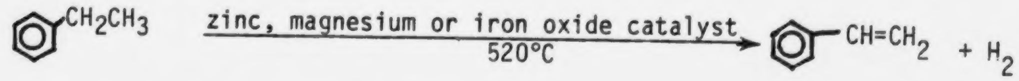
Olefins are prepared from their saturated hydrocarbons as shown in reaction 2.

The formation of butadiene from butane:

$$CH_3CH_2CH_2CH_3 \xrightarrow[600\text{-}620°C]{\text{chromia-alumina catalyst}} CH_2{=}CHCH{=}CH_2 + H_2(g) \qquad (2)$$

The major byproduct of all these reactions is hydrogen gas.

Styrene is the organic chemical described in the process description because emission data were readily available. Styrene is made from the dehydrogenation of ethylbenzene as shown in reaction 3.



9.2 DESCRIPTION OF DISCHARGES

Releases from a typical dehydrogenation process occur in wastewater, in gaseous emissions, and in solid residues.

fugitive emissions - occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains and cooling towers.

dehydrogenation section - pollutants are released when regenerating and purging the catalyst beds as air emissions, wastewater, and spent catalysts. Also air emissions occur from leaks in the reactors.

product cooling - using condensers, partial condensers and oil quenches result in contaminated liquid waste streams and vent gases.

product purification - using caustic scrubbers, degassers and water washes result in contaminated liquid waste streams.

product separation - absorbers, strippers and fractionating columns (both extractive and conventional distillations) result in fugitive and intermittent air emissions, solid tarry matter in bottoms at blowdown, contaminated liquid wastes containing products, and extractive solvents.

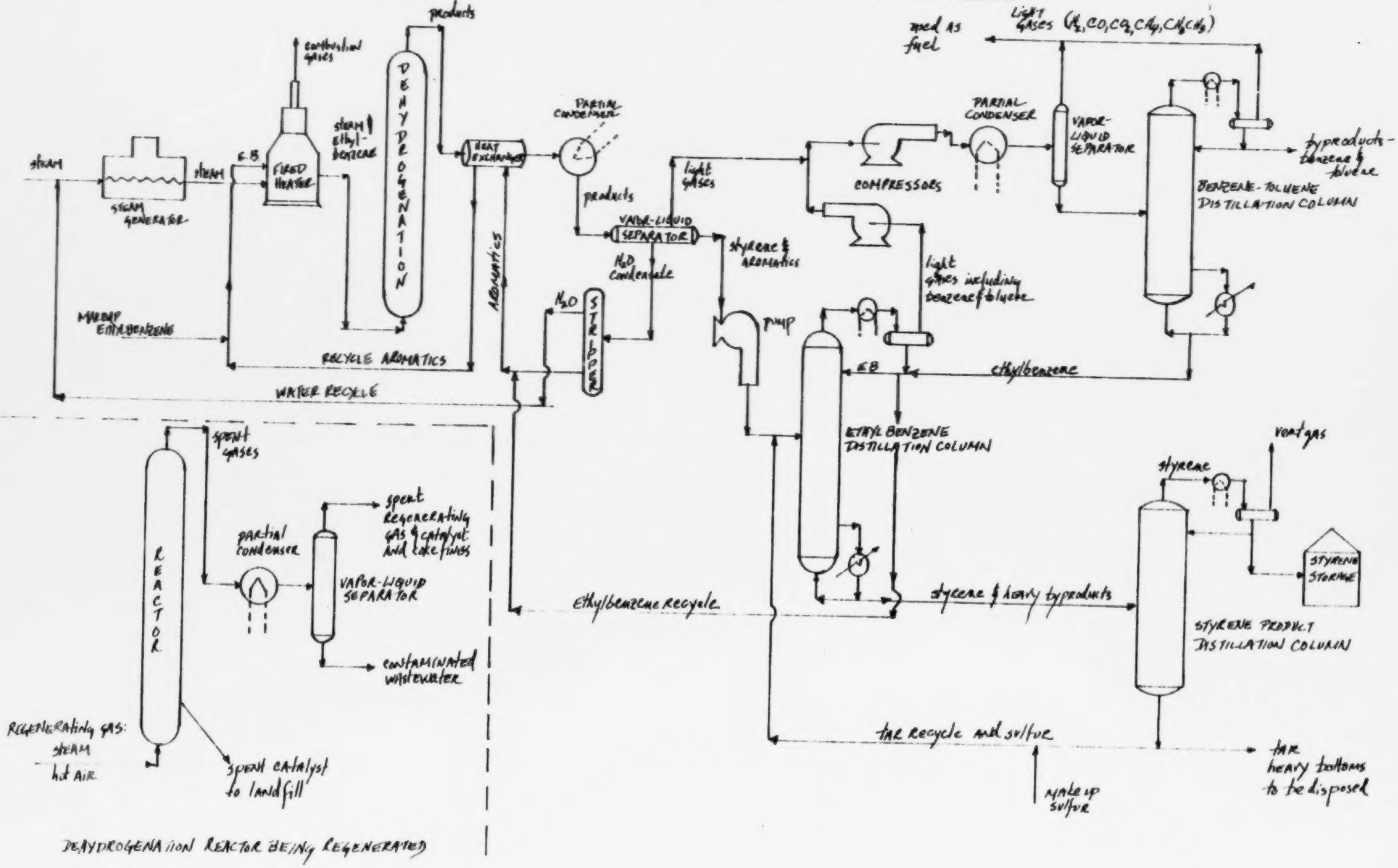
steam generation and cooling towers - contaminants released during operation and at blowdown.

9.3 PRODUCTION PROCESS - MANUFACTURE OF STYRENE BY DEHYDROGENATION

Polymer grade styrene is manufactured by dehydrogenation of ethylbenzene in a catalytic reactor. Most plants produce the ethylbenzene on site by alkylating benzene with ethylene. The reactants for the dehydrogenation are ethylbenzene and superheated steam. The reaction is an endothermic, vapor-phase reaction which takes place in a catalytic bed reactor at subatmospheric pressures. The resulting products are styrene, hydrogen, carbon monoxide, carbon dioxide, light hydrocarbon gases, benzene, toluene, and a heavy bottoms product.

The dehydrogenation process mainly involves a dehydrogenation reactor and distillation columns to separate the products. A detailed flow diagram is presented in Figure 9-2. Processing sequences may differ from company to company but generally they are: 1) dehydrogenation, 2) product cooling and vapor-liquid separation, 3) ethylbenzene distillation column, 4) styrene product distillation, and 5) benzene-toluene distillation column. Fresh ethylbenzene and superheated steam are combined with recycle ethylbenzene and charged to the dehydrogenation reactor. The dehydrogenation products are cooled and condensed and sent to the styrene monomer recovery section which consists of 3 distillation columns. The noncondensable products, hydrogen, carbon dioxide, methane, etc., are drawn off in a vapor-liquid separator preceding the distillation columns and used as fuel (except carbon dioxide). The first distillation column separates the light products from the heavy products. The overhead stream

FIGURE 9-2. PROCESS FLOW DIAGRAM FOR THE MANUFACTURE OF STYRENE BY DEHYDROGENATION



Source: This diagram was constructed from the description in UOP (1979) is mostly benzene, toluene and ethylbenzene, and the bottoms product consists of styrene and heavy bottoms product. The small amount of benzene and toluene produced by cracking in the dehydrogenation reaction is separated from the ethylbenzene for recycle by partial condensation, vapor-liquid separation, and a second distillation. The styrene monomer is separated in a third column from small amounts of tar and polymer formed during the operation. Inhibitors are added to minimize polymer formation. In the discussion of each process step, the potential sources of emissions are included.

9.3.1 Dehydrogenation

The dehydrogenation section consists of a steam generator, a fired heater, and catalytic dehydrogenation reactors. Fresh ethylbenzene, super heated steam and a recycle stream of ethylbenzene, benzene, and toluene are charged to a fired heater. The superheated mixture from the fired heater proceeds to the dehydrogenation reactors which are three to eight fixed-bed catalytic reactors arranged in parallel alternately performing the operations of reaction, regeneration, and purge. The dehydrogenation of ethylbenzene to styrene is a vapor-phase, endothermic reaction. The steam is used as a diluent to reduce the partial pressure of the styrene, to supply the heat consumed by the endothermic dehydrogenation reaction, and to enhance catalyst activity by burning off coke deposits. The resulting dehydrogenation products advance to the product cooling section.

9.3.1.1 Emissions from Dehydrogenation

The dehydrogenation reactors are alternately being used for reaction, regeneration, and purge. Catalyst beds need to be regenerated because carbon (coke) deposits occur on the catalyst surfaces. Carbon deposits result from decomposition of organic chemicals at such high temperatures. Regeneration of catalyst beds involves passing a hot regenerating gas, in this case steam and hot air, through the catalyst beds to remove any residual carbon from the catalyst surfaces. The coke is being combusted with steam and hot air to yield carbon dioxide and carbon monoxide. Complete burning is generally assumed but probably does not occur, and therefore carbon monoxide is released. The emissions that result are carbon dioxide, carbon monoxide, some hydrocarbon gases, coke fines and catalyst fines. If the regeneration gases are scrubbed with water to remove the coke and catalyst fines and condensable gases, this creates an intermittent wastewater stream which is discarded. Toxic oxygenated by-products of some catalyst systems may be vented to the atmosphere or discharged with wastewater (Hedley 1975).

When the catalyst life is completed, the packed-bed is purged. An average catalyst life is 2 years (Monsanto, Hydrocarbon Processing 1973). Whole beds of catalyst are removed and replenished. Spent catalyst is either landfilled or put into solution and used as a byproduct.

No emission data were found for the packed-bed columns during reaction. Since it is a vapor phase reaction, fugitive emissions will occur at valves, vents, seals, and leaks. Combustion gases from gas-fired heaters may be fairly high in nitrate (NO_x) content because of high-flame temperature and non-stoichiometric combustion control (Radian 1977). Sulfur emissions are low because most furnaces burn sulfur-free fuel (Radian 1977).

9.3.2 Product Cooling and Vapor-Liquid Separation

In product cooling, the dehydrogenation gases are cooled in a heat exchanger, partially condensed in a partial condenser, and separated in a vapor-liquid separator. The purpose of the heat exchanger is to recover heat and to prevent polymerization of styrene. Generally, there are a couple of heat exchangers; some are heating the ethylbenzene recycle stream and others are heating steam while cooling the dehydrogenation gases from 1100° F. The partial condenser only condenses the steam and heavy aromatics, including styrene and ethylbenzene. It is operated at subatmospheric pressures to aid in keeping benzene and toluene in the vapor phase.

The mixed phase advances to a vapor-liquid separator. The vapors are drawn off the top of the separator and the liquids fall to the bottom of the separator. The vapors are composed of hydrogen, carbon dioxide, carbon monoxide, methane, ethylene ethane, steam, and approximately 10 mole percent of benzene and toluene and a small amount of ethylbenzene and styrene (UOP, 1980). The vapors are sent to the benzene-toluene splitter, but the more volatile components are removed before reaching the splitter. The liquid phase, water, and heavy aromatics, including styrene and ethylbenzene, are separated in a product settler. The styrene, ethylbenzene, and other aromatics are pumped to the ethylbenzene distillation column. The condensed stream composed of 95 percent of the water present and some organics is sent to a stripper. The stripped water is sent to the steam generator, and the organics are recycled via a heat exchanger to the dehydrogenation reaction.

9.3.2.1 Emissions from Product Cooling and Vapor-Liquid Separation

The major release from the product cooling section would normally be the condensate stream-contaminated water coming off the vapor-liquid separator. However, in the reviewed UOP process, this stream is sent to a stripper and recycled and reused. In the heat exchangers and the partial condensers, the cooling waters will become contaminated because of leaks in the system. Fugitive emissions from valves, leaks, etc., will occur from every piece of equipment in the product cooling and vapor-liquid separation section.

9.3.3 Ethylbenzene Distillation Column

The ethylbenzene column separates the styrene and heavier aromatics from the ethylbenzene and lighter aromatics. It is called the ethylbenzene column because ethylbenzene is removed in the overhead vapors. The styrene and heavier aromatics are removed as the bottoms product and pumped to the styrene product distillation column. The overhead vapors proceed through a partial condenser and a vapor-liquid separator instead of the standard total condensers for distillation columns. Incomplete condensation is used to separate the ethylbenzene from the lighter gases including the majority of the benzene and toluene. The light gases proceed to the benzene-toluene splitter. The condensed ethylbenzene is refluxed back into the distillation column and recycled back to the dehydrogeneration section.

9.3.3.1 Emissions from Ethylbenzene Distillation Column

Fugitive emissions may result at vents, valves, seals, and leaks in the equipment. Intermittent emissions may occur at relief vents on fractionation towers.

9.3.4 Styrene Product Distillation Column

The styrene product distillation column separates the styrene from the heavy by-products, called tarry matter. Tarry matter which contains styrene trimer, stilbene, biphenylnaphthalene, phenanthrene, ethylphenanthrene, and others (Hedley 1975). Some of the tarry matter is removed and disposed of; the rest is recycled to the ethylbenzene distillation column. Hedley (1975) has reported that 14.1 pounds of tarry matter per ton of styrene are disposed of. Makeup sulfur is added to the recycle tarry matter to prevent polymeric materials from being formed.

The overhead vapors from the styrene product column are mostly styrene. Most of the overhead products are condensed in a partial condenser and separated as liquid in a gas-liquid separator. This resultant liquid is divided into reflux or a net styrene product stream. A small vapor stream resulting from air leaks and dissolved gases is drawn off in the gas-liquid separator and released to the air.

9.3.4.1 Emissions from Styrene Column

Fugitive emissions will occur at flanges, valves, seals, and leaks from the distillation column and its equipment. A vent gas from the gas-liquid separator as described above will be emitted. The cooling water in the partial condenser may become contaminated.

9.3.5 Benzene-Toluene Splitter

The light gases including the majority of the benzene and toluene proceed to the benzene-toluene splitter. These gases originate from the vapor-liquid separator after dehydrogenation and the overhead product from the ethylbenzene distillation column. Before reaching the benzene-toluene splitter, these gases are compressed and partially condensed to remove the light gases, hydrogen, carbon monoxide, carbon dioxide, methane, ethylene and ethane. The mixed phase from the partial condenser is separated in a vapor-liquid separator. The condensed liquid made up mainly of benzene and toluene continues to the benzene-toluene splitter. The light gases are used as fuel.

The benzene-toluene splitter is a small distillation column whose overhead product is benzene and toluene. The bottoms product is mostly styrene and ethylbenzene which are recycled back to the ethylbenzene column. As with the ethylbenzene column, the condensing section of the benzene-toluene splitter is a partial condenser and a vapor-liquid separator. The effect of this is to condense the benzene and toluene but draw off any uncondensed light gases that may have remained in the process. The light gases are sent to be used as fuel. The hydrogen may first be separated from the light gas fuels to be used in a hydrogenation unit. The benzene and toluene product may be further separated at which point the benzene will be recycled to the ethylbenzene alkylation unit and the toluene will be sold as a by-product.

9.3.5.1 Emissions from Benzene-Toluene Splitter

Fugitive emissions may result at vents, valves, seals, and leaks from every piece of equipment (partial condensers, vapor-liquid separators, and distillation columns). Intermittent emissions may occur at relief vents on fractionation towers. The cooling waters in the partial condenser will become contaminated with benzene and ethylbenzene.

Fugitive emissions may result from compressors especially at compressor seals. Polymer formation and fouling may occur. The compressors are flushed to dissolve the polymeric materials formed. This cleaning yields an intermittent liquid waste stream.

9.3.6 Other Processes

Two processes not discussed here, but are used by other dehydrogenation reactions, are caustic scrubbers/water wash and liquid-liquid extraction.

9.3.6.1 Caustic Scrubbers

Caustic scrubbers are used to remove any acid gases contained in the product gases. In a caustic wash, the product gases come in direct contact with the caustic solution. The acid gases react with the caustic to form a precipitate and water which fall to the bottom of the scrubber. The precipitate and water are sent to a settling tank. The precipitate is a salt; the water (spent caustic) may be contaminated with acid and base. A water wash generally follows a caustic wash. The water also comes in direct contact with the product gases. The spent caustic and spent water wash are degassed to remove product gases. The resultant gases from the degasser are vented, flared, or recycled. This degassing stream may be a continuous emission. The spent caustic and spent wash water are neutralized and ponded.

9.3.6.2 Extractive Distillation

Extractive distillation is used when two liquids with relatively close boiling points must be separated. A third solvent is added that will go into solution with one of the two liquids to be distilled. The boiling point of the solution will be different, and therefore the solution and the second liquid can be separated by conventional distillation. After extractive distillation, the two liquids in the solution must be separated in an absorber. The resulting product is distilled again for refinement.

Extractive distillation has similar wastes to conventional distillations. Fugitive emissions will occur at flanges, valves, seals, and leaks in the equipment. An intermittent emission may occur at relief vents on fractionator towers. The emissions will be composed of the liquids being separated and the extractive solvents.

9.4 SUMMARY OF EMISSIONS DATA

Table 9-2 summarizes the emissions and products from each step of styrene production by dehydrogenation. Table 9-3 shows the estimated releases found for other dehydrogenation reactions.

White (1980) Organic Chemical Manufacturing - Selected Process (Volume 9 & 10) evaluates the air emissions and possible control technologies for two dehydrogenation chemicals: linear alkyl benzenes and butadiene. Pertinent data were extracted and are presented in the following figures and tables.

Butadiene is produced by dehydrogenation of n-butane and n-butenes. Figure 9-3 is a flow diagram of the uncontrolled model plant for the production of butadiene by the n-butane dehydrogenation (HOUDRY) process. Table 9-4 shows the typical composition of the stream exiting the Houdry reactor before purification and separation. Table 9-5 demonstrates the volatile organic chemical emissions from uncontrolled and controlled dehydrogenation plants. Table 9-5 is to be used in conjunction with Figure 9-3; the letters in the stream designation column correspond to letters on Figure 9-3. The same presentation was done for the production of butadiene by oxidative dehydrogenation of n-butenes. Figure 9-4 and Tables 9-6 and 9-7 should be reviewed in the same manner as described above for the Houdry process.

Linear alkyl benzenes (LAB) are produced from n-paraffins (C_{10}-C_{14} mixtures) and benzene in a two-step sequence of reactions. The first step is dehydrogenating the n-paraffins to olefins, and the second step is alkylating the benzenes with the olefins. The process is called the LAB Olefin process, a flow diagram for which is pictured in Figure 9.5. White (1980) has evaluated the emission rates at which benzene and volatile organic chemicals (VOC) are emitted from the LAB Olefin process. These uncontrolled emission rates are tabulated in Table 9-8. Control technology and emission reduction were studied next by White

TABLE 9-2. SUMMARY OF RELEASES FROM EQUIPMENT USED IN DEHYDROGENATION OPERATIONS

	Air	Water	Land
Dehydrogenation reactor	Fugitive emissions will occur from valves, vents, seals, and leaks.		
	Releases from regenerating catalyst beds include carbon dioxide, carbon monoxide, some hydrocarbons, coke fines, and catalyst fines.	If regeneration gases are scrubbed with water to remove coke and catalyst fines and condensable gases, an intermittent waste water results.	Spent catalysts will be landfilled.
Fired heater	Combustion gases may be fairly high in nitrate content and may be sulfur content depending on fuel used.		
Cooling in heat exchanger		The cooling water will become contaminated due to leaks in the heat exchanger.	
Partial condenser		The cooling water will become contaminated due to leaks in the condenser.	
Vapor-liquid separator	Fugitive emissions from valves, seals, and leaks.		
Product-settler to separate water from organics		Water stream contains organics; some plants send this contaminated water through a stripper and recycle and reuse the water and the organics. Otherwise, the water stream is discarded; large pollution potential.	
Distillation columns	Fugitive emissions may result at vents, valves, seals, and leaks; intermittent emissions may occur at relief vents on distillation columns.		

TABLE 9-2. SUMMARY OF RELEASES FROM EQUIPMENT USED IN DEHYDROGENATION OPERATIONS (CONTINUED)

	Air	Water	Land
Compressors	Fugitive emissions, especially at compressor seals.	When flushing compressors, an intermittent waste water stream results.	
Caustic scrubbers	Gases from degassing stream.	Spent caustic and spent water waste are neutralized and ponded.	Salt precipitate.
Liquid-liquid extraction	Same as for distillation column; emissions will also include the extraction solvents.		

TABLE 9-3. ESTIMATED RELEASES FOUND IN SOME DEHYDROGENATION PROCESSES

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Styrene from ethylbenzene	- heavy ends and tarry matter	product settler	by-products	r	water	0.393[1]	NA	liquid	NA	NA
		superheater		r	water	5.9[1]	NA	liquid	NA	NA
		still bottom		r	land	7.05[1]	NA	solid	NA	NA
	- aromatics, phenol	process effluent	by-product	r	water	NA[4]	NA	liquid	NA	NA
Isoprene from tertiary amylenes from C_5 hydrocarbons	- sodium hydroxide	amylene recovery section - separation from C_5 hydrocarbons - separation vessel	reactants	r	water	3.05[2]	NA	liquid	NA	NA
	sodium sulfate					14[2]	NA	liquid		
	- n-hexane	amylene recovery section - amylene recovery column - liquid-liquid extraction	solvents	r	water	19[2]	NA	liquid	NA	NA
	- isoprene	dehydrogenation section - partial condenser	products	r	water	0.5[2]	NA	liquid	NA	NA
	amylene		by-products	r	water	1.5[2]	NA	liquid		
	- acetonitrile	isoprene recovery section - extractive distillation column	solvent	r	air	5[2]	NA	gas	NA	NA
Butadiene from n-butylenes	- pH	typical wastewater composition - 100 gallons/ton of product	waste water	r	water	9-9[3]	NA	liquid	NA	NA
	TOC					100-200 mg/l[3]	NA	liquid		
	filtered COD					250-375 mg/l[3]	NA	liquid		
	suspended solids					200-500 mg/l[3]	NA	liquid		
	total solids					3,000-4,000 mg/l[3]	NA	liquid		
Methyl ethyl ketone from sec-butyl alcohol	- methyl ethyl ketone	caustic scrubber and water wash	by-products	r	water	NA	NA	liquid	NA	NA
	reaction by-products					NA	NA	liquid		

TABLE 9-3. ESTIMATED RELEASES FOUND IN SOME DEHYDROGENATION PROCESSES (continued)

				Uncontrolled Emissions			Controlled Emissions			
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Acetaldehyde	Acetaldehyde	absorber vents	product from process emissions	r	air	0.228	11.8 [5]	gas	NA	NA
		product storage tanks	product from storage emissions	r	air	0.029	1.5 [5]	gas	NA	NA
		equipment leaks	product from fugitive	r	air	0.013	0.67 [5]	gas	NA	NA
	Ethylene	absorber vents	feedstock	r	air	NA	NA [5]	gas	NA	NA
	Ethane	absorber vents	feedstock	r	air	NA	NA	gas	NA	NA

Sources:

[1] Hedley et al. (1975). Based on 90,700 kkg/yr capacity.

[2] Hedley et al. (1975). Based on 36,300 kkg/yr capacity.

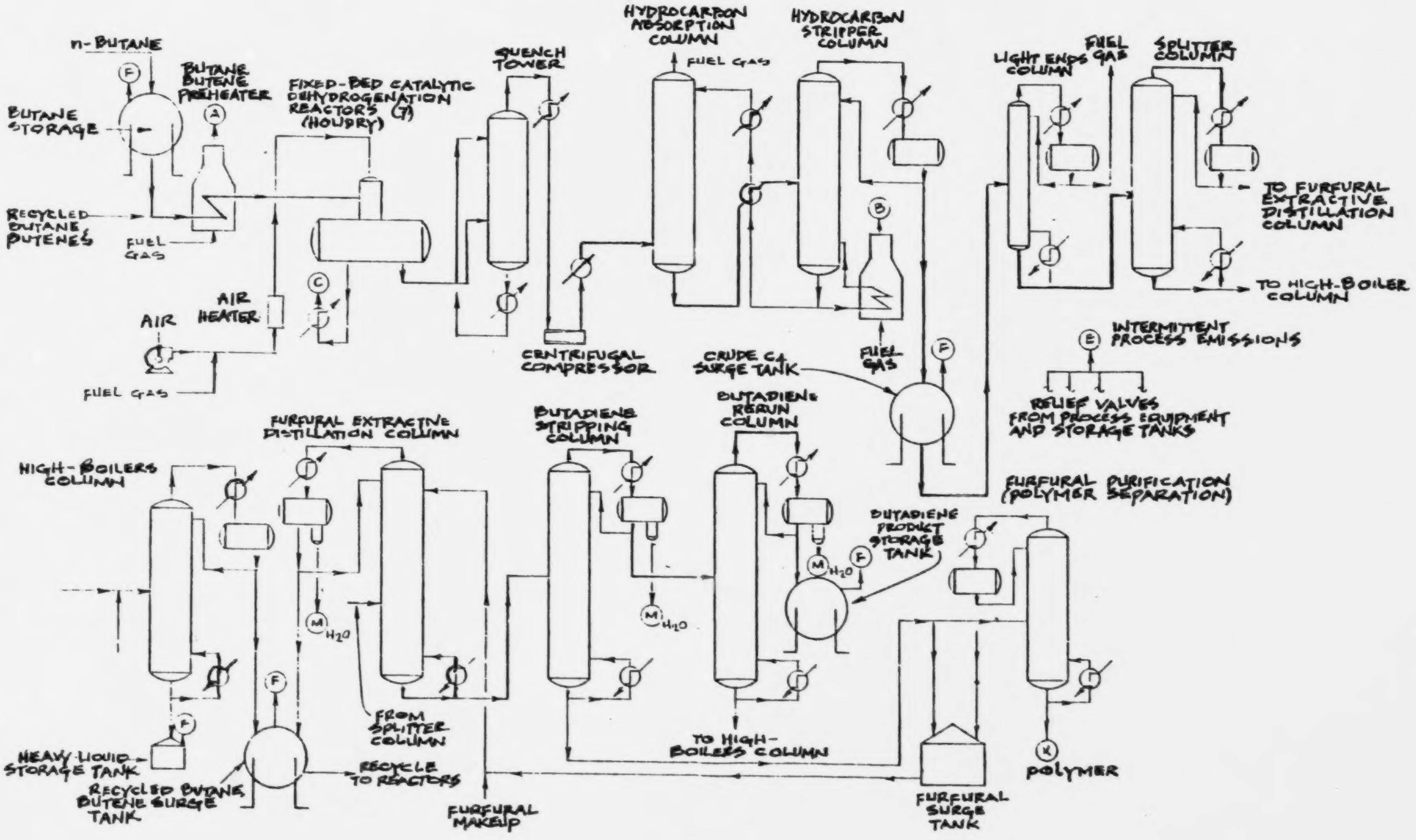
[3] Hedley et al. (1975). Based on 45,500 kkg/yr capacity.

[4] Wise and Farenthold, 1981. Concentration reported were greated than 0.5 ppm. Ethylbenzene is the feedstock.

[5] SAI, Vol. I (1981). Based on annual production of 453,600 kkg/yr.

+ Denotes that a release is routine (r) or accidental (a).

Figure 9-3. FLOW DIAGRAM OF UNCONTROLLED MODEL PLANT FOR PRODUCTION OF BUTADIENE BY n-BUTANE DEHYDROGENATION (HOUDRY) PROCESS


n-BUTANE
F
BUTANE STORAGE
BUTANE BUTENE PREHEATER
A
RECYCLED BUTANE, BUTENES
FUEL GAS
FIXED-BED CATALYTIC DEHYDROGENATION REACTORS (7) (HOUDRY)
AIR HEATER
AIR
FUEL GAS
C
QUENCH TOWER
CENTRIFUGAL COMPRESSOR
HYDROCARBON ABSORPTION COLUMN
FUEL GAS
HYDROCARBON STRIPPER COLUMN
B
FUEL GAS
CRUDE C4 SURGE TANK
F
LIGHT ENDS COLUMN
FUEL GAS
SPLITTER COLUMN
TO FURFURAL EXTRACTIVE DISTILLATION COLUMN
TO HIGH-BOILER COLUMN
E
INTERMITTENT PROCESS EMISSIONS
RELIEF VALVES FROM PROCESS EQUIPMENT AND STORAGE TANKS
HIGH-BOILERS COLUMN
F
HEAVY LIQUID STORAGE TANK
F
RECYCLED BUTANE BUTENE SURGE TANK
RECYCLE TO REACTORS
FURFURAL EXTRACTIVE DISTILLATION COLUMN
M H2O
FROM SPLITTER COLUMN
FURFURAL MAKEUP
BUTADIENE STRIPPING COLUMN
M H2O
BUTADIENE RERUN COLUMN
M H2O
F
BUTADIENE PRODUCT STORAGE TANK
TO HIGH-BOILERS COLUMN
FURFURAL PURIFICATION (POLYMER SEPARATION)
FURFURAL SURGE TANK
K
POLYMER

Source: White, 1980 (Volume 10)

TABLE 9-4. TYPICAL COMPOSITION OF n-BUTANE DEHYDROGENATION (HOUDRY) REACTOR EMISSIONS

Component	Molecular Formula	Composition (wt %)
Hydrogen	H_2	1.4
Carbon oxides	CO, CO_2	0.7
Methane	CH_4	0.7
Ethane	C_2H_6	0.3
Ethylene	C_2H_4	0.6
Propane	C_3H_8	0.1
Propylene	C_3H_6	1.0
n-Butane	C_4H_{10}	40.5
Isobutane	C_4H_{10}	1.0
Isobutene	C_4H_8	4.3
1-Butene	C_4H_8	12.7
Trans-2-butene	C_4H_8	13.6
Cis-2-butene	C_4H_8	11.3
1,3-Butadiene	C_4H_6	11.1
C_5's hydrocarbons		0.6
1,2-Butadiene	C_4H_6	Trace
Propadiene	C_3H_4	Trace
Methylacetylene	C_3H_4	Trace
Ethylacetylene	C_4H_6	Trace
Dimethylacetylene	C_4H_6	Trace
Vinylacetylene	C_4H_4	Trace
		100.0

Source: White 1980 (Volume 10)

TABLE 9-5. UNCONTROLLED AND CONTROLLED VOC EMISSION FROM BUTADIENE PRODUCTION BY DEHYDROGENATION OF n-BUTANE (HOUDRY PROCESS)

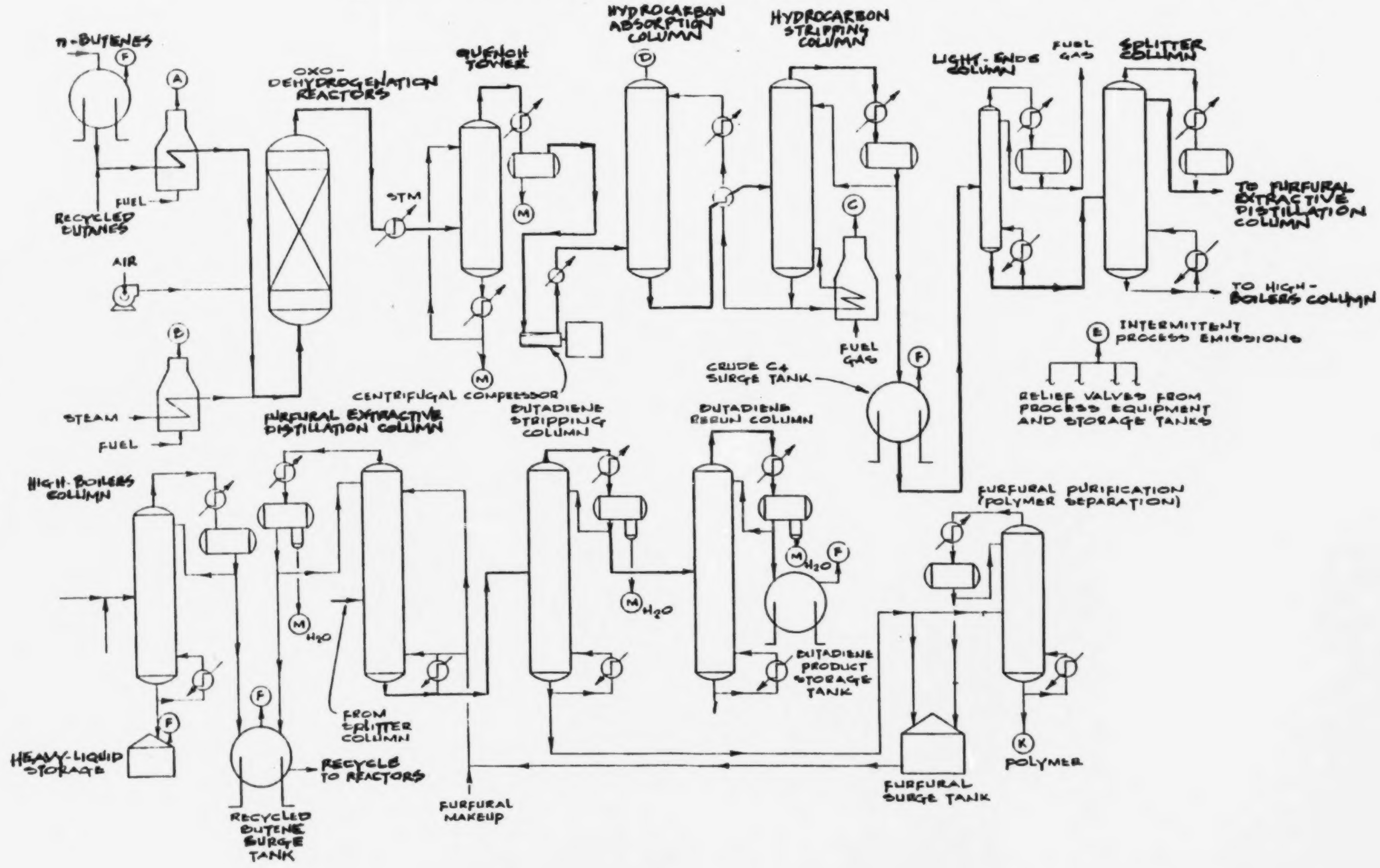
				Uncontrolled Emissions			Controlled Emissions	
Location	Source	Type of Release +	Receiving medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
(stream designation in Figure 9-3)								
Flue gas (A, B)	by-products	r	air	0.06	NA	gas	None	0.06
Reactor vent (C) (regeneration air)	by-products	r	air	5.5	NA	gas	Catalytic or thermal oxidation	0.44
Intermittent process emissions (E)	by-products	r	air	0.5	NA	gas	Elevated flare	0.03
Storage and handling (F)	products and reactants	r	air	0.1	NA	gas	None[a]	0.1
Secondary (K, M)	by-products	r	air	0.15	NA	gas	None	0.15
Fugitive	by-products	r	air	5.2	NA	gas	Detection and repair of major leaks plus mechanical seals	1.3
Total				11.5				2.1

Source: White (1980) (Volume 10), Report 7, p. IV-2. Based on 160,000 kkg/yr capacity.

[a] Pressurized storage tanks vented to the process are considered to be normal process conditions, not a separate emission control.

+Denotes that a release is routine (r).

FIGURE 9-4. FLOW DIAGRAM OF UNCONTROLLED MODEL PLANT FOR PRODUCTION OF n-BUTENES OXIDATIVE DEHYDROGENATION PROCESS


n-BUTENES
F
A
FUEL
RECYCLED BUTANES
AIR
B
STEAM
FUEL
OXO-DEHYDROGENATION REACTORS
STM
QUENCH TOWER
M
M
CENTRIFUGAL COMPRESSOR
HYDROCARBON ABSORPTION COLUMN
D
HYDROCARBON STRIPPING COLUMN
C
FUEL GAS
CRUDE C4 SURGE TANK
F
LIGHT-ENDS COLUMN
FUEL GAS
SPLITTER COLUMN
TO FURFURAL EXTRACTIVE DISTILLATION COLUMN
TO HIGH-BOILERS COLUMN
E
INTERMITTENT PROCESS EMISSIONS
RELIEF VALVES FROM PROCESS EQUIPMENT AND STORAGE TANKS
HIGH-BOILERS COLUMN
F
HEAVY-LIQUID STORAGE
FURFURAL EXTRACTIVE DISTILLATION COLUMN
M H2O
F
RECYCLED BUTENE SURGE TANK
RECYCLE TO REACTORS
FROM SPLITTER COLUMN
FURFURAL MAKEUP
BUTADIENE STRIPPING COLUMN
M H2O
BUTADIENE RERUN COLUMN
M H2O
F
BUTADIENE PRODUCT STORAGE TANK
FURFURAL PURIFICATION (POLYMER SEPARATION)
FURFURAL SURGE TANK
K
POLYMER

Source: White, 1980 (Volume 10)

TABLE 9-6. TYPICAL COMPOSITION OF n-BUTENE OXIDATIVE DEHYDROGENATION REACTOR EFFLUENT

Component	Molecular Formula	Composition (wt %)
Oxygen	O_2	1.0
Nitrogen	N_2	15.8
Carbon oxides	CO, CO_2	3.0
Water	H_2O	65.0
Methane	CH_4	0.1
C_2's		0.3
C_3's		0.4
n-Butane	C_4H_{10}	0.4
Isobutane	C_4H_{10}	0.6
Isobutene	C_4H_8	1.1
1-Butene	C_4H_8	1.9
Trans-2-butene	C_4H_8	1.7
Cis-2-butene	C_4H_8	1.4
1,3-Butadiene	C_4H_6	7.2
C_5's		0.1
1,2-Butadiene	C_4H_6	Trace
Propadiene	C_3H_4	Trace
Methylacetylene	C_3H_4	Trace
Ethylacetylene	C_3H_4	Trace
Dimethylacetylene	C_4H_6	Trace
Vinylacetylene	C_4H_4	Trace

Source: White, 1980 (Volume 10)

TABLE 9-7. UNCONTROLLED AND CONTROLLED VOC EMISSION FROM BUTADIENE PRODUCTION BY OXIDATION DEHYDROGENATION OF n-BUTENES

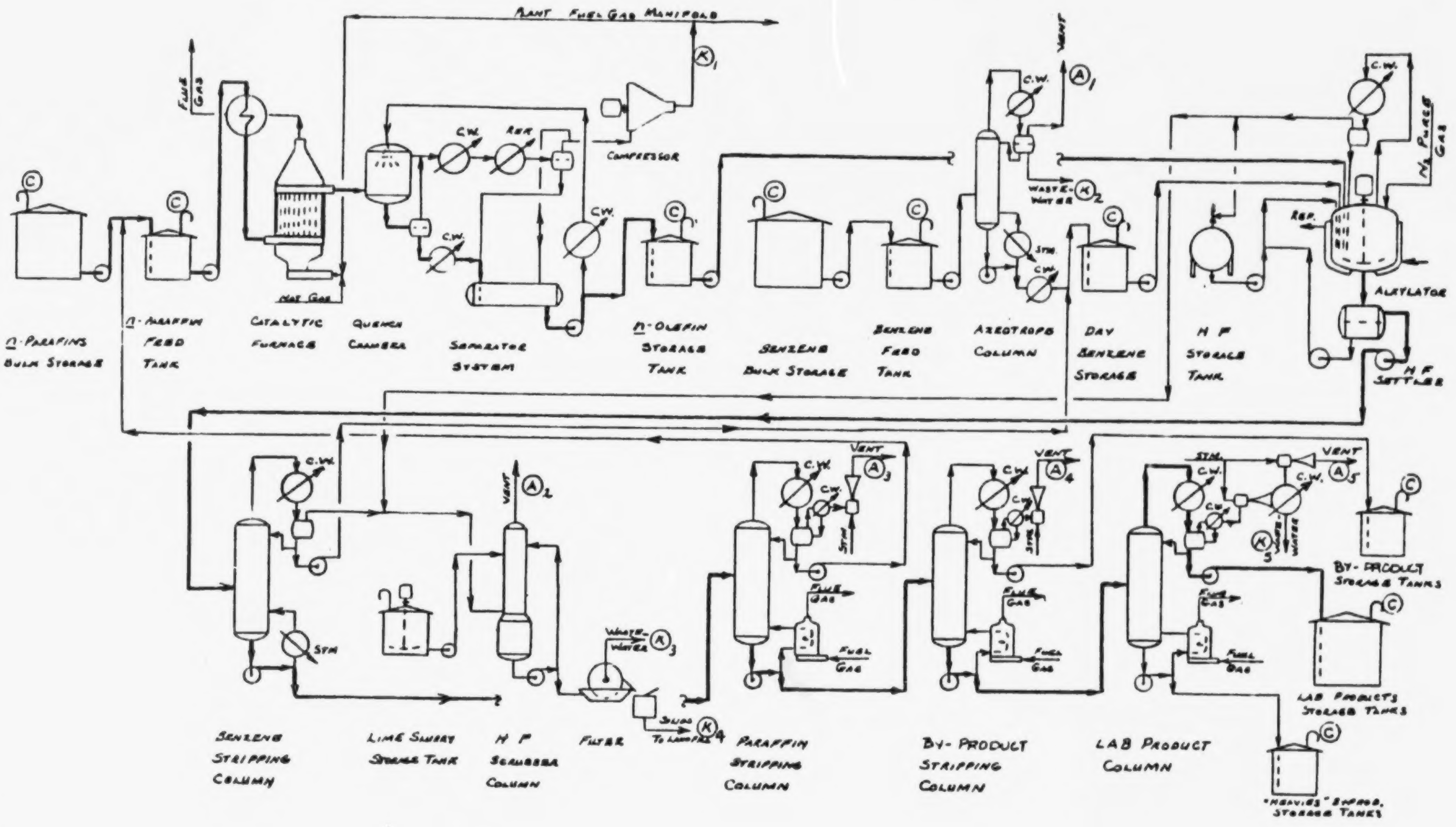
				Uncontrolled Emissions			Controlled Emissions	
Location	Source	Type of Release +	Receiving medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
(stream designation in Figure 9-4)								
Flue gas (A, B, C)	by-products	r	air	0.06	NA	gas	None	0.06
Absorption column column vent (D)	by-products	r	air	5.0	NA	gas	Catalytic or thermal oxidation	0.25
Intermittent process emissions (E)	by-products	r	air	0.5	NA	gas	Elevated flare	0.03
Storage and handling (F)	products and reactants	r	air	0.1	NA	gas	None[a]	0.1
Secondary (K, M)	by-products	r	air	0.75	NA	gas	Reactor wastewater stripper-flare vented vapor	0.24
Fugitive	by-products	r	air	5.2	NA	gas	Detection and repair of major leaks plus mechanical seals	0.13
Total				11.6				2.0

Source: White(1980) (Volume 10), Report 7, p. IV-3. Based on 160,000 kkg/yr capacity.

[a] Pressurized storage tanks vented to the process are considered to be normal process conditions, not a separate emission control.

+Denotes that a release is routine (r).

Figure 9-5. FLOW DIAGRAM FOR LAB OLEFIN PROCESS MODEL PLANT WITH UNCONTROLLED EMISSIONS



Source: White, 1980 (Volume 7)

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TABLE 9-8. UNCONTROLLED AND CONTROLLED BENZENE AND TOTAL VOC EMISSION FOR A 90 Gg/YR MODEL PLANT USING THE LAB OLEFIN PROCESS

				Uncontrolled Emissions				Controlled Emissions			
Location (stream designation in Figure 9-5)	Source	Type of Release +	Receiving medium	Quantity kg/kkg product		Rate kg/hr		Form	Control Technology	Quantity kg/kkg product	
				Benzene	Total VOC	Benzene	Total VOC			Benzene	Total VOC
Benzene azeotrope column vent (A_1)	by-products	r	air	3.7[1]	3.7[1]	0.038[1]	0.038[1]	gas	Used as fuel	0.00074[2]	0.00074[2]
Hydrogen fluoride scrubber column vent (A_2)	by-products	r	air	11[1]	11[1]	0.11[1]	0.11[1]	gas	Used as fuel (Alt. 1)	0.0022[2]	0.0022[2]
								gas	Flare (Alt. 2)	1.1[2]	1.1[2]
Paraffin stripping column vent (A_3)	by-products	r	air		88[1]		0.9[1]	gas	Surface condenser		7.0[2]
By-product stripping column vent (A_4)	by-products	r	air		1[1]		0.01[1]	gas	None[a]		1.0[2]
LAB product column vent (A_5)	by-products	r	air		0.0014[1]		0.000014[1]	gas	None[a]		0.0014[2]

Source: [1] White (1980) (Volume 7), Report 7, p. IV-4. Based on 90,000 kkg/yr capacity.

[2] Ibid, p. V-3.

[a] Jet exhaust surface condenser recommended for suppression of steam plume.

+Denotes that a release is routine (r).

(1980), and the results of their study are shown in Table 9-8. Monsanto is the only company operating a LAB Olefin process in the U.S. Tables 9-9 and 9-10 show the control devices and techniques currently in use by Monsanto and the estimated emissions from the Monsanto LAB Olefin Plant.

Although these estimated emissions are for particular chemicals, other organic chemicals will have similar equipment with similar wastes. All processes will have a dehydrogenation reactor; a product cooling, purification and separation train; valves, pumps, etc.; cooling towers; and stream generators similar to the plants described. The wastes will vary because of different operating conditions, volatilities, solubilities, and maintenance of equipment.

TABLE 9-9 . CONTROL DEVICES AND TECHNIQUES CURRENTLY USED IN THE LAB OLEFIN PROCESS

Source	Stream Designation (Fig. 9-5)	Emission Control Devices and Techniques*
Benzene azeotrope control vent	A_1	None
Hydrogen fluoride scrubber column vent	A_2	Vent gases sent to flare for combustion
Paraffin stripping column vent	A_3	Vent condenser used to minimize VOC to vacuum jet; no condenser used on jet exhaust
Lights stripping column vent	A_4	Vent condenser used to minimize VOC to vacuum jet
LAB product column vent	A_5	Vent condenser used to minimize VOC to vacuum jets; surface condenser used as intercondenser between second-stage jet and final steam jet
Storage and handling emissions	C	Refrigerated vent condenser used to reduce emissions from fixed-roof benzene storage tank used to feed process
Fugitive emissions	J	Mechanical single and double seals used on centrifugal pumps; quality of maintenance on valves, etc., not known, but plant appeared to be clean and neat; special precautions used during plant shutdowns and turnarounds
Secondary emissions	K	Plant wastewater streams combined, put through an enclosed skimming tank to remove floating organics; then skimmed, filtered wastewater fed to a deep-well injection system for disposal; filtered solids are then sent to land fill; organic skimmings are recovered and returned to the process or are burned as fuel

---

*Used by Monsanto

Source: White, 1980 (Volume 7)

TABLE 9-10. ESTIMATED EMISSIONS FROM MONSANTO LAB PLANT

	Emission Ratio (g/Mg)[a]			
	Potential		Actual Existing	
Source	Benzene	VOC	Benzene	VOC
Benzene drying vent	3.7	3.7	3.7	3.7
HF scrubber vent	11.0	11.0	1.1	1.1
Paraffin stripper vent		88.0		88
Lights stripper vent		1		1
LAB prod. column vent		0.0014		0.0014
Storage and handling	602	668	141.1	203.1
Fugitive emissions	4.9	20.3	4.9	20.3
Secondary emissions	71	142.0	16	33
Total emissions	692.6	933	166.8	350.2

[a] g of emission per Mg of LAB produced.

Source: White, 1980 (Volume 7). Based on 109,000 kkg/yr capacity.

REFERENCES

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Co., Inc.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Morrison, R. T. and R. N. Boyd. 1976. Organic Chemistry, 3rd ed. Boston, Massachusetts: Allyn and Baron, Inc.

Radian Corp. 1977. Industrial Process Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Research Triangle Park, North Carolina: Industrial Environmental Research Lab, U.S. EPA.

SAI. 1981. Human Exposure to Atmospheric Concentrations of Selected Chemicals (Vol. I). Prepared for the Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina.

Shreve, R. N. 1967. Chemical Process Industries, 3rd ed. New York, New York: McGraw Hill Book Company.

Union Carbide Corp. 1980. U.S. Patent Δ4,220,803. Catalytic Dehydrogenation of Ethanol for the Production of Acetaldehyde and Acetic Acid.

Vande Mond. T. J. Stamicarbon. 1981. U.S. Patent Δ4,250,118. Process for Preparation of Cyclohexanone.

Ward, D. J. 1978. U.S. Patent Δ4,113,787. Aromatic Hydrocarbon Dehydrogenation Process, UOP, Inc.

Wetherold, R. G., D. D. Rosebrook, and B. A. Tichenor. 1981. Assessment of Atmospheric Emissions from Petroleum Refining. Research Triangle Park, North Carolina: U. S. Environmental Protection Agency.

White, R.E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volumes 6-10. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028a-e.

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SECTION 10

DEHYDROHALOGENATION

10.0 INTRODUCTION

In the process of dehydrohalogenation, a hydrogen atom and a halogen atom are removed from one or more feedstocks to obtain a new chemical. In commercial operation, the halogen atom is usually chlorine.

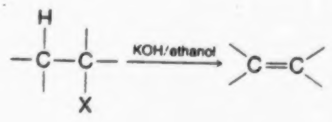
Some dehydrohalogenation processes use catalysts such as pyridine and mercuric chloride. A typical dehydrohalogenation train includes a reactor and a purification system.

Figure 10-1 is a typical process flow diagram. The principal organic chemicals manufactured by dehydrohalogenation are listed in Table 10-1.

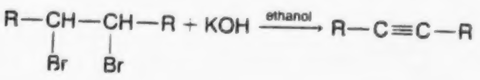
10.1 GENERAL CHEMISTRY

Dehydrohalogenation is an elimination reaction. The elements of a hydrogen halide (H-X) are removed from the feed. The hydrogen that is eliminated is one from a carbon adjacent to the carbon bearing the halogen. The common reactions are as follows:

(1) alkylhalide ——→ alkene + water + halide ion

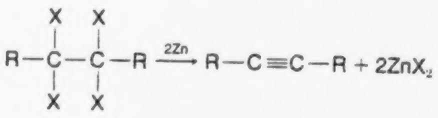


(2) alkyl dihalide ——→ alkynes



$$\mathrm{R{-}\underset{Br}{CH}{-}\underset{Br}{CH}{-}R + KOH \xrightarrow{ethanol} R{-}C{\equiv}C{-}R}$$

(3) tetrahalides



$$\mathrm{R{-}\overset{X}{\underset{X}{C}}{-}\overset{X}{\underset{X}{C}}{-}R \xrightarrow{2Zn} R{-}C{\equiv}C{-}R + 2ZnX_2}$$

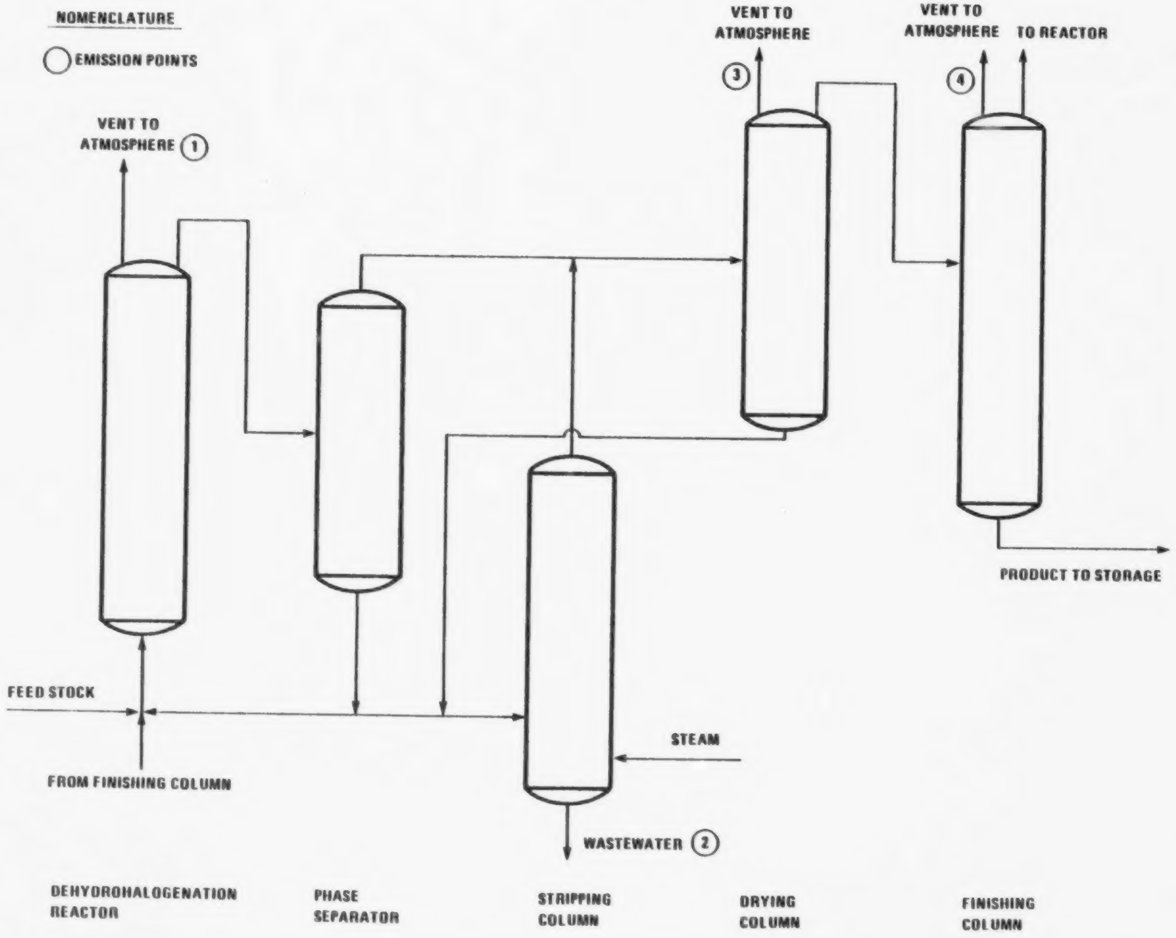


FIGURE 10-1 A TYPICAL DEHYDROHALOGENATION PRODUCTION PROCESS

TABLE 10-1. DEHYDROHALOGENATION PRODUCTS AND THEIR PRODUCTION IN 1979[1,2]

Product	Amount kkg	Feedstock	Other Required Processes
2-(2,4-Dichlorophenoxy) propionic acid (2,4-DP)	NA	α-chloropropionic acid (2,4-Dichlorophenol)	condensation
N-Isopropyl-N'-phenyl-p-phenylenediamine	28,436*	acetone aniline p-chloronitrobenzene	alkylation condensation hydrogenation
2-(2-Methyl-4-chlorophenoxy) propionic acid (MCPP)	NA	α-chloropropionic acid; 4-chlorocresol	condensation
Polycarbonate resins	127,800[3]	bisphenol A phosgene	phosgenation polymerization
Vinyl chloride monomer (VCM)	2,925,000[4]	acetylene ethane chlorine	halogenation oxyhalogenation
Vinyl chloride monomer (VCM)	2,925,000[4]	ethylene chlorine	halogenation oxyhalogenation
Vinyl chloride monomer (VCM) Hydrogen chloride	2,925,000[4]	ethylene dichloride	none
Vinyl chloride monomer (VCM)	2,925,000[4]	naphtha chlorine	halogenation oxyhalogenation
Vinylidene chloride	98,000[5]	vinyl chloride	halogenation

Sources: [1] Herrick 1979.
[2] USITC 1979.
[3] SRI 1981, 80% of January 1, 1981 capacity.
[4] Chemical & Engineering News, August 3, 1981, 1980 production.
[5] White 1980 , 80% of 1979 reported capacity.

*Includes all substituted p-phenylenediamine

Note: Dehydrohalogenation is not always the major method of production of these chemicals.

(4) halide reaction with a alkoxide

$$RO^{-}Na^{+} + CH_3CH_2\text{-}X \longrightarrow CH_2{=}CH_3 + ROH + NaX$$

A specific example of dehydrohalogenation is the production of vinyl chloride monomer (VCM). Ethylene dichloride is dehydrochlorinated to VCM, as shown in the following equation:

$$ClCH_2CH_2Cl \xrightarrow[480\text{-}510°C]{\text{catalyst}} CH_2 = CHCl + HCl$$

14.2 DESCRIPTION OF DISCHARGES

Releases from a typical dehydrohalogenation process occur as fugitive emissions, as reactor off-gases, as column wastes, as catalyst recovery residue, and as storage and handling emissions.

Fugitive - pressure relief valves, pump seals, compressor seals, drains, and cooling towers.

Process - reactor off-gases.

Purification - column vents, column waste streams, filter residue, and catalyst recovery residue.

Storage and Handling - vents from feed tanks, product tanks, and loading.

10.3 PRODUCTION OF VINYLIDENE CHLORIDE AND RESULTING EMISSIONS

Vinylidene chloride can be produced by the chlorination of vinyl chloride and the dehydrochlorination of the chlorination intermediate by the following reactions:

$$\underset{\text{(vinyl chloride)}}{CH_2 = CHCl} + \underset{\text{(chlorine)}}{Cl_2} \longrightarrow \underset{\text{(1,1,2-trichloroethane)}}{ClCH_2 - CHCl_2}$$

$$\underset{\text{(1,1,2-trichloroethane)}}{ClCH_2 - CHCl_2} + \underset{\text{(sodium hydroxide)}}{NaOH} \longrightarrow \underset{\text{(vinylidene chloride)}}{CH_2 = CCl_2} + \underset{\text{(sodium chloride)}}{NaCl} + \underset{\text{(water)}}{H_2O}$$

The dehydrohalogenation reaction is carried out in the liquid phase at a temperature of about 100°C, with a relatively dilute (5 to 10 wt %) sodium hydroxide solution. Product yields for the dehydrohalogenation reaction are believed to range from 85 to 90 percent.

The following discussion is based on information from White (1980) and is divided into these sections: (1) dehydrochlorination reactor and resulting emissions, (2) phase separator and stripping column and resulting emissions (3) drying column and finishing column and resulting emissions, and (4) storage, handling, and futitive emissions. Figure 10-2 is a flow diagram for a dehydrohalogenation process in which vinylidene chloride is produced from 1,1,2-trichloroethane.

10.3.1 Dehydrochlorination Reactor

Concentrated sodium hydroxide solution (Stream 1) is diluted with water (Stream 2) to 5 to 10% concentration and is combined with 1,1,2-trichloroethane feed (Stream 3), with unreacted feed (Stream 16) recycled from the distillation section of the process, and with recycled sodium hydroxide-salt solution (Stream 8). The combined feed stream (4) is further mixed to provide dispersal of the insoluble organic phase in the aqueous phase before it is fed to the dehydrochlorination reactor. The reactor is continuously purged with nitrogen (Stream 5) to prevent the accumulation of monochloroacetylene impurity in the vinylidene chloride product.

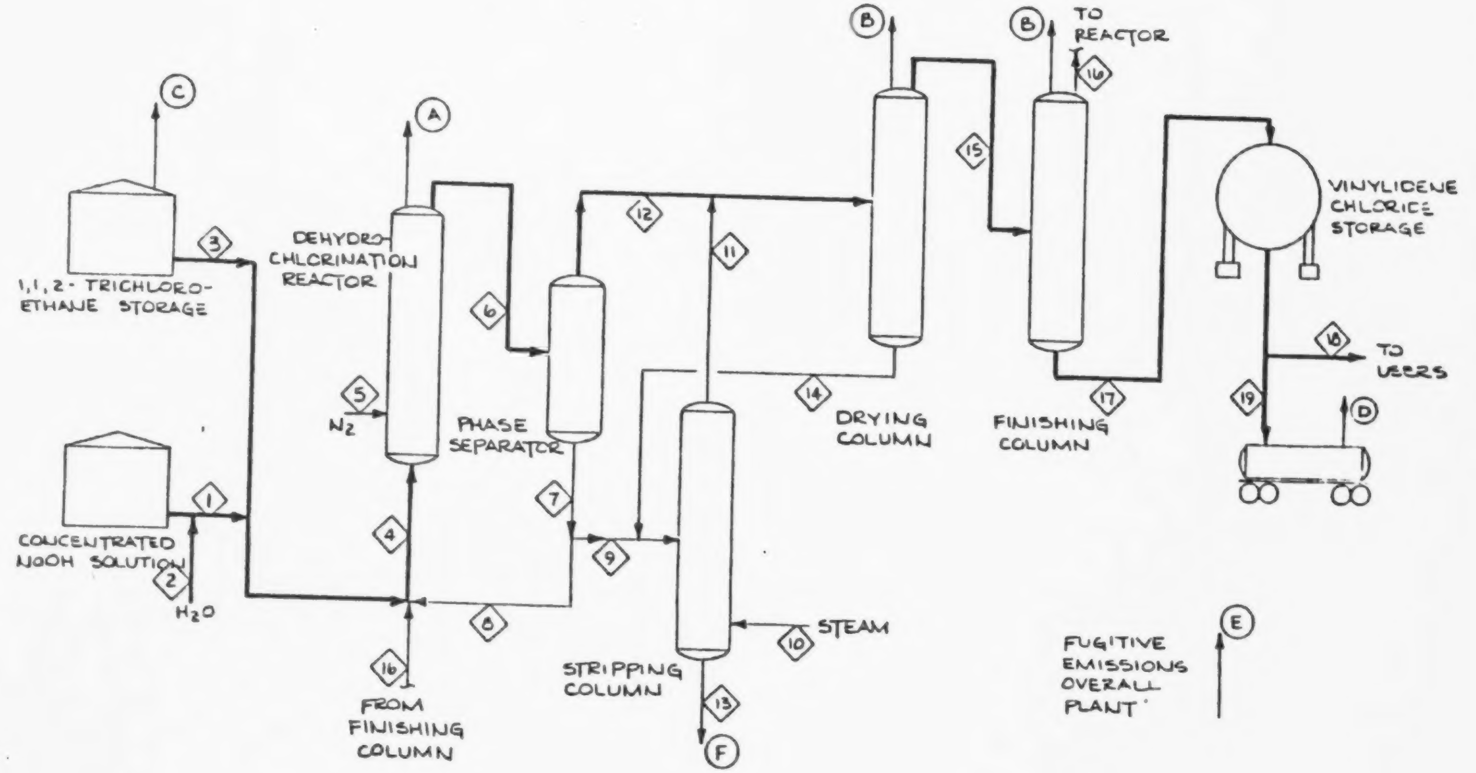
10.3.1.1 Emissions

The nitrogen purge results in a process emission source (Vent A) which releases primarily noncondensable gases, including vinylidene chloride, monochloroacetylene, and nitrogen.

10.3.2 Phase Separator and Stripping Column

The two-phase reactor effluent (Stream 6) is separated into two phases in a phase separator. The aqueous phase (Stream 7), composed of a sodium hydroxide-salt solution saturated with organic compounds, is split. One fraction (Stream 8) is recycled to the reactor. The other fraction

FIGURE 10-2. FLOW DIAGRAM FOR VINYLIDENE CHLORIDE FROM 1,1,2-TRICHLOROETHANE



Source: White 1980.

(Stream 9) is combined with the bottom stream (14) from the drying column and feed to the stripping column, where steam (Stream 10) is introduced countercurrently to strip most of the dissolved organics from the aqueous phase. The organics (Stream 11) are removed overhead and are combined with the organic phase (Stream 12) from the phase separator. The combined stream is fed to the drying column.

10.3.2.1 Emissions

The stripped aqueous phase is removed as the bottom stream (Stream F) from the stripping column. The stream is discharged to the wastewater treatment system, and the contained VOC are desorbed.

10.3.3 Drying Column and Finishing Column

The drying column bottom stream (14), which contains most of the residual water, is recycled to the stripping column. The drying-column overhead (Stream 15) goes to the finishing column. The finishing column overhead (Stream 16), composed primarily of unreacted 1,1,2-trichloroethane, is recycled to the reactor. The refined vinylidene chloride product is removed as the bottom (Stream 17) and transferred to storage in pressurized tanks. From storage, the vinylidene chloride may be transferred by pipeline for internal use (Stream 18) or loaded (Stream 19) into tank trucks for off-site consumption.

10.3.3.1 Emissions

The distillation column vents release primarily noncondensable gases.

10.3.4 Storage, Handling, and Fugitive Emissions

Storage emissions (Vent C) are the emissions from storage of 1,1,2-trichloroethane. With pressurized tanks used for vinylidene chloride storage, no significant emissions from product storage occur. Handling emissions (Vent D) result from the loading of vinylidene chloride into tank trucks and railroad tank cars. Fugitive emissions (Vent E) occur when leaks develop in valves, in pumps, or in compressor seals. When process pressures are higher than the cooling water pressures, VOC can leak into the cooling water and escape as fugitive emissions from the cooling tower.

10.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided in Table 10-2 for the following manufacturing processes:

- Polycarbonate resins
- Vinyl chloride and hydrogen chloride
- Vinylidene chloride (consult Figure 10-2 in conjunction with Table 10-2

No emissions data have been found for any other dehydrohalogenation manufacturing process.

TABLE 10-2. ESTIMATED RELEASES FOUND IN SOME DEHYDROHALOGENATION PROCESSES

						Uncontrolled Emissions			Controlled Emissions		
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product	Stream Design.
Polycarbonate	sodium chloride	catalyst (pyridine) recovery section-azeotrope column waste	by-product	r	water	760[1]	NA	liquid	NA	NA	
	raw materials and solvents	reaction vessel	feed	r	air	NA	NA	gas	NA	NA	
	solvents & resins	storage & handling	feed, product	r	air	NA	NA	gas	NA	NA	
Vinyl chloride	chlorinated C2's, chloromethanes	process effluent	by-product	r	water	NA[5]	NA	liquid	NA	NA	
	hydrogen chloride	tail gas absorber	by-product	r	air	0.1[1]	NA	gas	NA	NA	
Hydrogen chloride	vinyl chloride	tail gas absorber	product	r	air	5.0[1]	NA	gas	NA	NA	
	1,2-dichloroethylene	tail gas absorber	by-product	r	air	0.15[1]	NA	gas	NA	NA	
	1,1-dichloroethylene	tail gas absorber	by-product	r	air	0.4[1]	NA	gas	NA	NA	
	acetylene	tail gas absorber	by-product	r	air	1.5[1]	NA	gas	NA	NA	
	ethylene dichloride	filter solids	feed	r	land	0.8[1]	NA	solid	NA	NA	
	tars (as C_2HCl)	filter solids	by-product	r	land	0.05[1]	NA	solid	NA	NA	
	solids (as C)	filter solids	by-product	r	land	0.2[1]	NA	solid	NA	NA	
Vinylidene chloride	chlorinated C2's, chloromethanes	process effluent	by-product	r	water	NA[5]	NA	liquid	NA	NA	
	vinylidene chloride	reactor vent	product	r	air	6.2[2]	NA	gas	incineration	NA	A
	monochloroacetylene	reactor vent	by-product	r	air	0.9[2]	NA	gas	incineration	NA	A
	nitrogen	reactor vent	feed	r	air	4.0[2]	NA	gas	incineration	NA	A
	VOC	reactor vent	NA	r	air	7.1[2]	NA	gas	incineration	0.14[2]	A
	VOC	distillation vent	NA	r	air	0.7[2]	NA	gas	aqueous scrubber	0.07[2]	B
	sodium hydroxide	vinylidene chloride	feed	r	water	45.5[1]	NA	liquid	NA	NA	F
	sodium chloride	separation column	by-product	r	water	605.5[1]	NA	liquid	NA	NA	F
	vinylidene chloride	distillation vent gas	by-producct	r	air	0.7[4]	NA	gas	NA	NA	
	nitrogen	(estimated composition)	by-product	r	air	0.7[4]	NA	gas	NA	NA	

Sources: [1] Hedley 1975. Based on 9,100 kkg/yr capacity.

[2] IBID. Based on 90,700 kkg/yr capacity.

[3] IBID. Based on 13,500 kkg/yr capacity.

[4] White 1980. Vol. 8, Report 4, p. VI-19, p. V-7, p. IV-20. Based on 90,000 kkg/yr capacity.

[5] Wise and Fahrenthold, 1971. Taken from Table 3. Pollutant concentration at least 0.5 ppm. Feedstock is 1,2-dichloroethane.

[6] See notes. In this case, feedstock is 1,1,2-trichloroethane.

REFERENCES

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides, and Explosives Industries. U.S.Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, C. M. Moscowitg, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Company, Inc.

Herrick, E. C. J. A. King, R. P. Ouellette, and P. N. Cheremisinoff. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Key Chemicals: Vinyl Chloride, in Chemical & Engineering News, August 3, 1981, Vol. 59, No. 31, p. 10.

Monsan, R. S. and J. C. Sholton. 1974. Fundamentals of Organic Chemistry. New York: McGraw-Hill Book Company.

Solomons, T. W. Graham. 1978. Organic Chemistry, revised printing. New York: John Wiley and Sons.

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

U.S. ITC. 1979. United States Production and Sales. Synthetic Organic Chemicals. U.S. Department of Commerce.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 10. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028e.

Wise, Hugh E. Jr., and Paul D. Fahrenthold. November 1981. Predicting Priority Pollutants from Petrochemical Processes, Environmental Science and Technology, 15, (11), pp. 1292-1304.

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SECTION 11

ESTERIFICATION

11.0 INTRODUCTON

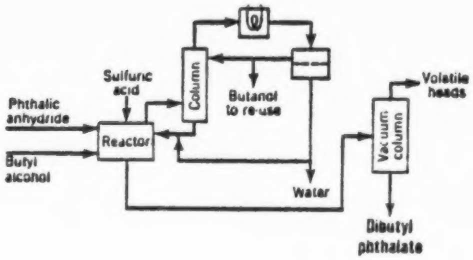
A carboxylic acid is converted into an ester when heated with an alcohol in the presence of a mineral acid such as sulfuric acid or hydrogen chloride. The process, called esterification, can be batch or continuous, liquid- or vapor-phase (Kirk-Othmer 1980).

The manufacture of dialkyl phthalates is an example of the batch process (Figure 11-1). Dialkyl phthalates are manufactured by esterifying phthalic anhydride with the appropriate alcohols in the vapor phase in the presence of a catalyst such as sulfuric acid. The reactor is equipped with an agitator and internal steam coils. Reaction temperature is 150 to 200°C. An azeotrope of alcohol and water is formed and goes through a distillation column to recover and recycle the alcohol. The crude product is discharged from the reactor and sent to a purification column. Here the volatile impurities are removed as vapors and are condensed. The purified product exits as bottoms (Faith et al. 1965).

Ethyl acetate, like most esters, can be produced by batch or continuous process (Figure 11-2). Continuous esterification is favored in large volume production. To produce ethyl acetate by continuous process, acetic acid, ethanol, and sulfuric acid are sent through a preheater to an esterifying column. The mixture refluxes and the distillate comes off as overhead, containing 20% product, excess alcohol, and water, which then is sent to a separating column.

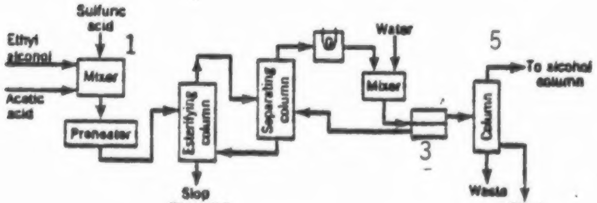
In the separating column, the mixture is refluxed and an azeotrope, of which 83% is product, and it exits as overhead. The bottoms of this

FIGURE 11-1 MANUFACTURE OF DIBUTYL PHTHALATE FROM PHTHALIC ANHYDRIDE AND ALCOHOL BY ESTERIFICATION



Source: Faith et al. 1965.

FIGURE 11-2 MANUFACTURE OF ETHYL ACETATE FROM ETHYL ALCOHOL AND ACETIC ACID BY ESTERIFICATION



or 5* overhead vent
6* bottoms

Source: Faith et al. 1965.

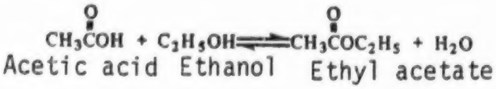
*For additional columns

separating column contain sulfuric acid. The overhead is sent to a mixer where it is blended with water. This mixture exits the mixer and settles in a decanter. The aqueous layer, which is on the bottom, is sent back to the separating column. The top layer goes to a drying column where ethyl acetate containing all remaining water and alcohol is distilled and removed as overhead, condensed, and sent to a second separating column. The bottoms contain 95 to 99% ester (Faith et al. 1965).

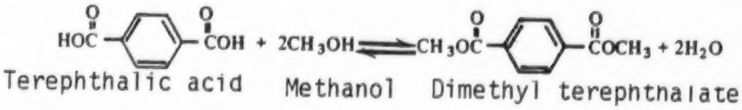
Esterification products and their 1980 production levels are found in Table 11-1.

11.1 GENERAL CHEMISTRY

Esterification is forming an ester from an organic acid and an alcohol by exchanging the ionizable hydrogen atom of the acid for an organic radical (Herrick et al. 1979).

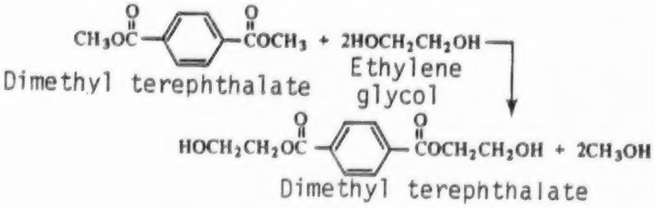


$$CH_3\overset{O}{C}OH + C_2H_5OH \rightleftharpoons CH_3\overset{O}{C}OC_2H_5 + H_2O$$



These reactions are reversible because the catalyst, hydrogen ion, that catalyzes the forward esterification reaction also catalyzes the reverse reaction, hydrolysis. Direct esterification, however, has the advantage of being a single-step synthesis (Morrison and Boyd 1973).

One alcohol is capable of displacing another alcohol from an ester. Transesterification involves the reaction of an ester and an alcohol to form a different ester.



This reaction can involve an acid or base catalyst.

TABLE 11-1. ESTERIFICATION PRODUCTS

Product	Amount*	Feedstock	Other Required Processes Oxidation
Acrylic acid & acrylate esters	714,136	propylene alcohols	oxidation
n-Butyl acetate	63,503	acetic acid n-butyl alcohol	
n-Butylbenzyl phthalate	NA	benzyl alcohol n-butyl alcohol phthalic anhydride	
Di-n-butyl phthalate	NA	n-butyl alcohol phthalate anhydride	
Diethyl phthalate	NA	ethyl alcohol phthalic anhydride	
Diheptyl phthalate	NA	heptyl alcohol phthalic anhydride	
Diisodecyl phthalate	NA	isodecyl alcohol phthalic anhydride	
Dimethyl phthalate	NA	methyl alcohol phthalic anhydride	
Dimethyl terephthalate	1,542,214 (feedstock not specified)	methyl alcohol terephthalic acid	
Dimethyl terephthalate		methyl alcohol p-xylene	oxidation
Di-n-octyl phthalate	NA	phthalic anhydride n-octyl alcohol	
Dioctylphthalate (2-ethylhexyl phthalate)	NA	2-ethylhexyl alcohol phthalic anhydride	

TABLE 11-1. ESTERIFICATION PRODUCTS (Cont.)

Product	Amount*	Feedstock	Other Required Processes Oxidation
Ethyl acetate	94,347	acetic acid ethyl alcohol	
Ethyl acetoacetate	NA	acetic acid	pyrolysis
Ethyl acrylate	NA	ethyl alcohol	oxidation
Isopropyl acetate	19,958	acetic acid isopropyl alcohol	
Methyl acetate	NA	acetic acid methyl alcohol	
Methyl acetonacetate	NA	acetic acid	pyrolysis
Methyl methacrylate	413,676	acetone hydrogen cyanide methyl alcohol	hydrocyanation hydrolysis sulfonation
Methyl methacrylate	NA	isobutylene methyl alcohol	oxidation
p-Oxybenzoic acid α p-Oxybenzoic butyrate	NA	butyl alcohol carbon dioxide phenol	carboxylation
Polyethylene terephthalate	257,640 (barrier resins) 177,808 (film)	ethylene glycol terephthalic acid	polymerization
Triacetate polymer (cellulose triacetate)	NA	acetic acid cellulose	
Tributyrin (glyceral tributyrate)	NA	n-butyric acid α glycerol	

Source: SRI 1981; Herrick et al. 1979.

*SRI lists amounts in plant capacities. For this table, the capacities were multiplied by 0.8.

Alkyl sulfonates, another form of ester, are formed from sulfonyl chlorides and alcohols:

$$\underset{\text{A sulfonic acid}}{ArSO_2Cl} + \underset{\text{An alcohol}}{ROH} \xrightarrow[\text{or pyridine}]{\text{aqueous OH}^-} \underset{\text{An alkyl sulfonate}}{ArSO_2OR} + Cl^- + H_2O$$

11.2 DESCRIPTION OF DISCHARGES

Releases from an esterification process will occur as fugitive and particulate gaseous emissions, liquid wastes, and solid residues. The major sources of contamination are (1) gaseous emissions from the vents on feed tanks and purification columns which pull off excess feedstock and by-products and (2) liquid emissions in wastestreams from the reactor and purification column containing excess feedstock, catalyst, and by-products.

Fugitive gaseous emissions - may occur from valves, pump seals, compressor seals, pressure relief valves, and drains.

Feed tank - gaseous excess feedstock will be released through a vent on the mix tank.

Purification column - excess feedstock and by-products are released through vents in the gaseous form, and in the liquid form they are washed out in a wastestream along with catalyst fines.

Heavy ends column - a sludge containing by-products, catalyst fines, and additives is removed from the heavy ends column to waste disposal (usually a landfill).

11.3 DESCRIPTION OF AN EXAMPLE PRODUCTION PROCESS: DIMETHYL TEREPHTHALATE MANUFACTURE

The manufacture of dimethyl terephthalate (DMT) by the esterification of terephthalic acid by methanol consists of four major steps: 1) esterification, 2) methanol recovery, 3) methanol purification, and 4) dimethyl terephthalate purification. Figure 11-3 illustrates this process. For each part, the decription highlights the emissions associated with that step of the process.

11.3.1 Esterification

Crude terephthalic acid (TPA) and methanol are mixed in slurry mix tanks. TPA, a solid, is insoluble in methanol. The slurry that is formed is pumped to a continuous reactor, where, at moderate temperatures and pressures, esterification occurs to form dimethyl terephthalate (DMT) and water. A liquid purge stream is drawn off as bottoms and sent to nonvolatile waste disposal. The crude DMT that is formed is sent to purification (White 1980).

11.3.1.1 Emissions

The vent on the slurry mix tanks releases excess gaseous feedstock. Sludge is purged from the bottom of the reactor and sent to an incinerator. Fugitive emissions may occur at pumps, flanges, and valves (White 1980).

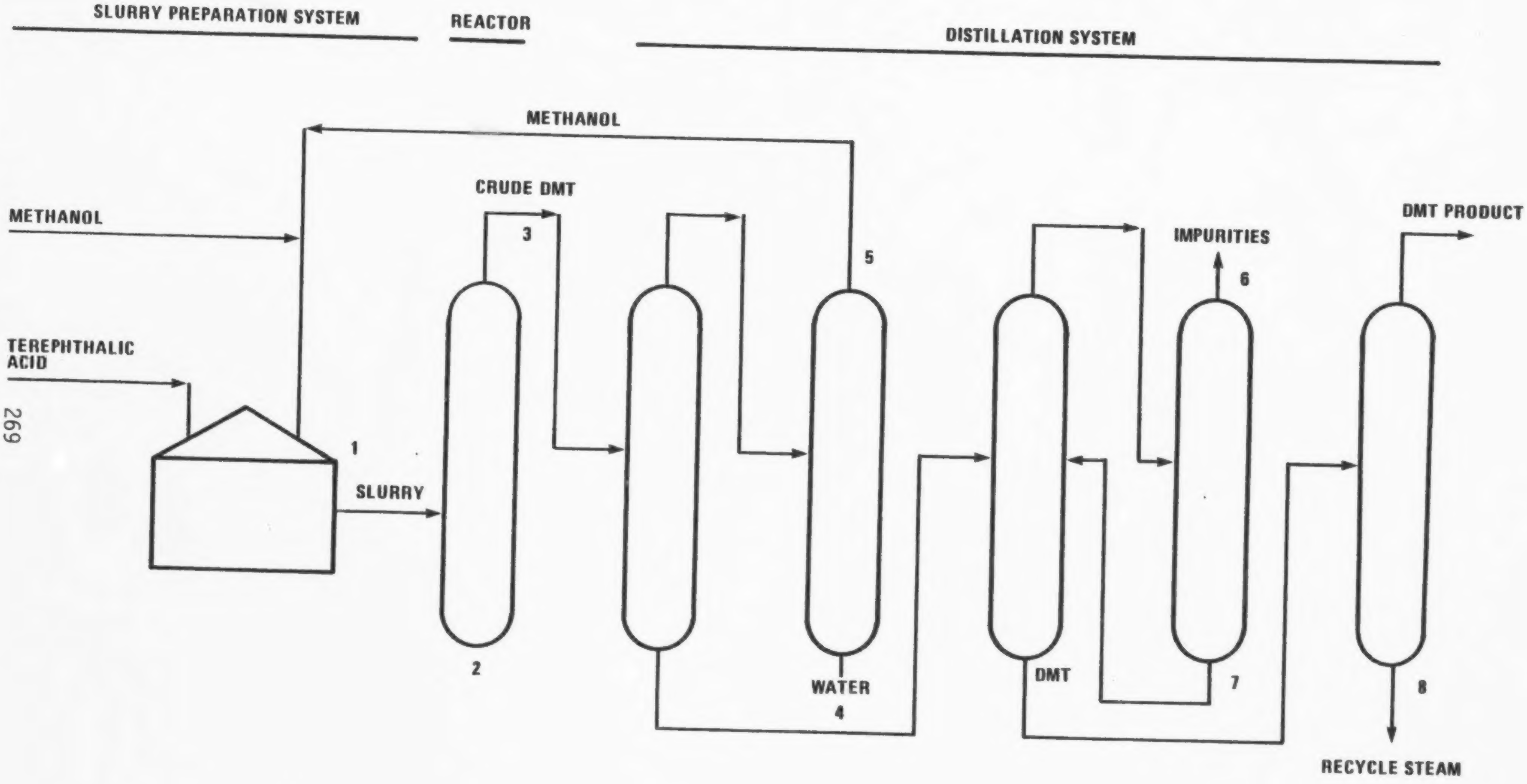
11.3.2 Methanol Recovery Still

The product stream from the reactor contains excess methanol; water, dimethyl ether and other low boilers, methyl p-toluate and methyl p-formyl benzoate; and DMT. This mixture enters a methanol recovery still, where methanol and the o-xylene-water azeotrope formed during esterification are removed as overhead and sent to a methanol flash still. The bottoms contain DMT which goes to further purification (White 1980).

11.3.2.1 Emissions

Fugitive emissions may occur at pumps, flanges, and valves (White 1980).

FIGURE 11-3 MANUFACTURE OF DIMETHYL TEREPHTHALATE



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Fugitive gaseous emissions	- may occur from valves, pump seals, compressor seals, pressure relief valves, and drains.
Feed tank	- gaseous excess feedstock will be released through a vent on the mix tank.
Purification column	- excess feedstock and by-products are released through vents in the gaseous form, and in the liquid form they are washed out in a wastestream along with catalyst fines.
Heavy ends column	- a sludge containing by-products, catalyst fines, and additives is removed from the heavy ends column to waste disposal (usually a landfill).

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11.3.1.1 Emissions

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11.3.2 Methanol Recovery Still

The product stream from the reactor contains excess methanol; water, dimethyl ether and other low boilers, methyl p-toluate and methyl p-formyl benzoate; and DMT. This mixture enters a methanol recovery still, where methanol and the o-xylene-water azeotrope formed during esterification are removed as overhead and sent to a methanol flash still. The bottoms contain DMT which goes to further purification (White 1980).

11.3.2.1 Emissions

Fugitive emissions may occur at pumps, flanges, and valves (White 1980).

11.3.3 Methanol Purification

The overhead methanol and o-xylene-water azeotrope enter a methanol flash still, where methanol, o-xylene, and other low boilers are taken overhead. This mixture enters a low boiler still (not shown) which distills off dimethyl ether and other low boilers as overhead for use as fuel. The bottoms contain methanol which is returned to the slurry tanks. Water is drawn off as bottoms of the methanol flash still and sent to wastewater treatment (White 1980).

11.3.3.1 Emissions

The bottoms from the methanol flash still are removed as a waste stream. This waste stream contains methanol, DMT product, and water. A vent on this still emits volatile organic chemicals. Fugitive emissions may occur at valves, pumps, and flanges (Hedley et al. 1975; White 1980).

11.3.4 DMT Purification

The bottoms of the methanol recovery still, containing DMT, are sent through a series of distillation columns. From the first column in this series, DMT exits as bottoms to a final distillation column where pure DMT product exits as overhead. The overhead from the first DMT purification column enters a column which removes impurities such as methyl p-toluate and benzoate as overhead to an incinerator (White 1980).

11.3.4.1 Emissions

Impurities are removed as overhead from the second distillation column and sent to an incinerator. The final product column releases a waste stream containing catalyst fines, excess feedstock, and by-products. Fugitive emissions may occur at valves, pumps and flanges (White 1980; Hedley et al. 1975).

11.4 SUMMARY OF EMISSION DATA

Emissions data are provided for the following manufacturing processes:

- Dimethyl terephthalate (Table 11-2)
- Ethyl acrylate (Table 11-3)
- Methyl methacrylate (Table 11-4)
- Polyethylene terephthalate (Table 11-5)
- Isopropyl acetate (Table 11-6)
- Ethyl acetate (Table 11-7)
- Dimethyl phthalate (Table 11-8)
- Diisodecyl phthalate (Table 11-9)
- Diethyl phthalate (Table 11-10)
- n-Butyl acetate (Table 11-11)

The emissions sources for Table 11-2 are found by consulting Figure 11-3; those for Tables 11-3 through 11-5 are found in Figure 11-2.

TABLE 11-2. CHARACTERIZATION OF EMISSIONS FROM THE DIMETHYL TEREPHTHALATE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Refer to Fig. 11-3)*	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Methanol	methanol column wastewater-4	feedstock	r	water	12[1]	NA	liquid	NA	NA
	light ends column-7		r	water	trace[1]	NA	liquid	NA	NA
Dimethyl terephthalate	MeOH column wastewater-4	product	r	water	0.27[1]	NA	liquid	NA	NA
	light ends column-7		r	water	8.5[1]	NA	liquid	NA	NA
	product column-8		r	water	54[1]	NA	liquid	NA	NA
Methyl p-formylbenzoate	light ends column-7	by-product	r	water	0.72[1]	NA	liquid	NA	NA
Acetic acid	light ends column-7	feedstock (for terephthalic acid)	r	water	trace[1]	NA	liquid	NA	NA
Terephthalic acid	product column-8	feedstock	r	water	0.9[1]	NA	liquid	NA	NA
Methylhydrogen terephthalate	product column-8	by-product	r	water	29.8[1]	NA	liquid	NA	NA
Zinc dust	product column-8	catalyst fines	r	water	1.17[1]	NA	solid	NA	NA
Antimony oxide	product column-8	catalyst fines	r	water	1.17[1]	NA	solid	NA	NA
Isophthalic acid	product column-8	by-product	r	water	trace[1]	NA	liquid	NA	NA
p-Formylbenzoic acid	product column-8	by-product	r	water	trace[1]	NA	liquid	NA	NA

TABLE 11-2. CHARACTERIZATION OF EMISSIONS FROM THE DIMETHYL TEREPHTHALATE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Total VOC	slurry mix tank vent-1	feedstocks, product, and by-product	r	air	1.0[2]	30.72[2]	gas	o-xylene absorber	0.04[3]
	reactor bottoms-2		r	air	0.038[2]	1.17[2]	gas	o-xylene scrubber	0.011[3]
	product condenser vent-3		r	air	0.34[2]	10.44[2]	gas	refrigerated condenser	0.065[3]
	MeOH flash still vent-5		r	air	0.02[2]	0.61[2]	gas	none	0.02[3]
	pumps, compressors, valves		a	air	0.66[2]	20.43[2]	gas	detection and correction of major leaks	0.175[3]
Phenol	process effluent	various	r	water	NA[4]	NA	water	various	NA

*Point 6 is considered a point of emissions, but no data were available.

+Denotes that release is routine (r) or accidental (a)

[1] Hedley et al. 1975, p. 251.

[2] White, Vol. 7, Report 5, p. IV-8. Based on production capacity of 269,000 kkg/yr.

[3] White, Vol. 7, Report 5, p. V-5.

[4] Wise and Fahrenthold 1981. (Table 3). Pollutant concentrations are at least 0.5 ppm. Feedstock were methanol and TPA.

TABLE 11-3. CHARACTERIZATION OF EMISSIONS FROM THE ETHYL ACRYLATE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Refer to Fig. 11-2)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Polymers	product column bottoms-4	by-product	r	water	11.9[1]	NA	liquid (in solution)	NA	NA
Hydroquinone	product column bottoms-4	additive	r	water	13.75[1]	NA	liquid (in solution)	NA	NA
Ethanol	product column overhead-5	feedstock	r	air	2.65[1]	NA	gas	NA	NA
Ethylacrylate	product column overhead-5	product	r	air	1.6[1]	NA	gas	NA	NA
Ethylacetate	product column overhead-5	by-product	r	air	5.25[1]	NA	gas	NA	NA
Sodium carbonate	product column overhead-5	additive	r	air	0.265[1]	NA	gas	NA	NA

+Indicates that release is routine (r) or accidental (a).

[1] Hedley et al. 1975. p.155. Based on 13,608 kkg/yr capacity.

TABLE 11-4. CHARACTERIZATION OF EMISSIONS FROM THE METHYL METHACRYLATE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Refer to Fig. 11-2)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Acetone	vent on feed tank-1	feedstock	r	air	29.5[1]	NA	gas	NA	NA
	light ends column-4		r	water	26.45[1]	NA	liquid	NA	NA
Hydrogen cyanide	Vent on feed tank-1	feedstock	r	air	3.15[1]	NA	gas	NA	NA
	light ends column-4		r	water	0.25[1]	NA	liquid	NA	NA
Hydroquinone	light ends column-4	additive	r	water	0.25[1]	NA	liquid (in solution)	NA	NA
	MeOH column sludge-6		r	land	1.125[1]	NA	solid	NA	NA
Methylmethacrylate	light ends column-4	product	r	water	1.8[1]	NA	liquid	NA	NA
Methanol	MeOH column bottoms-6	feedstock	r	water*	12[1]	NA	liquid	NA	NA
Polymers	MeOH column bottoms-6	by-product	r	water*	6.05[1]	NA	liquid (in solution)	NA	NA
	MeOH column sludge-6		r	land	75[1]	NA	solid	NA	NA
Ammonia	MeOH column bottoms-6	by-product	r	water*	10.35[1]	NA	liquid	NA	NA
Ammonium acetate	MeOH column bottoms-6	by-product	r	water*	0.9[1]	NA	liquid	NA	NA
Ammonium cyanide	MeOH column bottoms-6	by-product	r	water*	19.45[1]	NA	liquid	NA	NA
Ammonium methacrylate	MeOH column bottoms-6	by-product	r	water*	19.9[1]	NA	liquid	NA	NA
Ammonium sulfate	MeOH column bottoms-6	by-product	r	water*	2832[1]	NA	liquid	NA	NA
Sodium sulfate	filter cake-3	by-product	r	land	101.5[1]	NA	solid	NA	NA

+Indicates that release is routine (r) or accidental (a).

*May also go to ammonium sulfate recovery process.

[1] Hedley et al. 1975. p.130. Based on 15,876 kkg/yr capacity.

TABLE 11-5. CHARACTERIZATION OF EMISSIONS FROM THE POLYETHYLENE TEREPHTHALATE PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Refer to Fig. 11-2)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Ethylene glycol	cooler effluent (not shown)	feedstock	r	water	5.9[1]	NA	liquid	NA	NA
	glycol column-4		r	land	0.475[1]	NA	liquid	NA	NA
	glycol finishing column-6		r	land	1.9[1]	NA	liquid	NA	NA
Polyethylene glycols	glycol column-4	by-product	r	land	23.1[1]	NA	liquid	NA	NA
	glycol finishing column-6		r	land	0.095[1]	NA	liquid	NA	NA
Sodium hydroxide & sodium bisulfite	glycol column-4	additives	r	land	0.095[1]	NA	solid	NA	NA
Miscellaneous (organic and inorganic)	glycol finishing column-6	product, by-products, feedstocks, additives	r	land	0.095[1]	NA	solid & liquid	NA	NA

+Indicates that release is routine (r) or accidental (a).

[1] Hedley et al. 1975. p.247. Based on 37,648 kkg/yr capacity.

TABLE 11-6. CHARACTERIZATION OF EMISSIONS FROM THE ISOPROPYL ACETATE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release†	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Isopropanol	NA	feedstock	r	NA	NA	NA	NA	NA	NA
Isopropyl acetate	NA	product	r	NA	0.5	NA	NA	NA	NA
Dilute sulfuric acid	NA	feedstock	r	water	0.5	NA	liquid	NA	NA

Source: EPA 1981, Organic, Chemical Producers Data Base.

†Emissions are routine (r).

TABLE 11-7. CHARACTERIZATION OF EMISSIONS FROM THE ETHYL ACETATE MNAUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release†	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Ethanol	NA	feedstock	r	NA	2.5	NA	NA	NA	NA
Ethyl acetate	NA	product	r	NA	2.5	NA	NA	NA	NA
Dilute sulfuric acid	NA	feedstock	r	water	NA	NA	liquid	NA	NA

Source: EPA 1981, Organic Chemical Producers Data Base.
†Emissions are routine (r).

TABLE 11-8. CHARACTERIZATION OF EMISSIONS FROM THE DIMETHYL PHTHALATE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Phthalic anhydride	NA	feedstock	r	NA	1.0	NA	NA	NA	NA
Methanol	NA	feedstock	r	water	1.0	NA	gas/liquid	NA	NA
Dilute coustic	NA	scrubber	r	water	NA	NA	liquid	NA	NA
Methyl phthalate	NA	by-product	r	water	NA	NA	liquid	NA	NA
Sulfates	NA	catalyst	r	water	NA	NA	NA	NA	NA

Source: EPA 1981, Organic Chemical Producers Data Base.

+Emissions are routine (r).

TABLE 11-9. CHARACTERIZATION OF EMISSIONS FROM THE DIISODECYL PHTHALATE

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Phthalic anhydride	NA	feedstock	r	NA	1.0	NA	NA	NA	NA
Isodecanol	NA	by-product	r	water	1.0	NA	liquid	NA	NA
Dilute caustic	NA	scrubber	r	water	NA	NA	liquid	NA	NA
Isodecyl phthalate monoester	NA	by-product	r	water	NA	NA	liquid	NA	NA
Sulfates	NA	catalyst	r	water	NA	NA	liquid	NA	NA

Source: EPA 1981, Organic Chemical Producers Data Base.

+Emissions are routine (r).

TABLE 11-10. CHARACTERIZATION OF EMISSIONS FROM THE DIETHYL PHTHALATE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Ammonia	NA	impurities	r	water	NA	NA	liquid	NA	NA
Cadmium	NA	catalyst	r	water	.0001	NA	liquid	NA	NA
Chloride	NA	catalyst	r	water	.104	NA	liquid	NA	NA
Copper	NA	catalyst	r	water	.064	NA	liquid	NA	NA
Cyanide	NA	impurities	r	water	NA	NA	liquid	NA	NA
Ethanol	NA	feedstock	r	air/water	NA	NA	gas/liquid	NA	NA
Dilute Caustic	NA	scrubber	r	water	NA	NA	liquid	NA	NA
Ethyl phthalate monoester	NA	by-product	r	water	NA	NA	liquid	NA	NA
Iron	NA	catalyst	r	water	.0025	NA	liquid	NA	NA
Oil	NA	feedstock	r	water	8.04	NA	liquid	NA	NA
Phenol	NA	by-product	r	water	NA	N	liquid	NA	NA
Sulfates	NA	catalyst	r	water	1.33	NA	liquid	NA	NA
Total phosphorous	NA	catalyst	r	water	.0021	NA	liquid	NA	NA
Total chromium	NA	catalyst	r	water	NA	N	liquid	NA	NA
Zinc	NA	catalyst	r	water	.0025	NA	liquid	NA	NA

Source: EPA 1981, Organic Chemical Producers Data Base.

+Emissions are routine (r).

TABLE 11-11. CHARACTERIZATION OF EMISSIONS FROM THE n-BUTYL ACETATE MANUFACTURING PROCESS

				Uncontrolled Emissions				Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
n-Butyl acetate	NA	product	r	air/water	0.5	NA	gas/liquid	NA	NA
Butanol	NA	feedstock	r	NA	0.5	NA	NA	NA	NA
Acetic acid	NA	feedstock	r	water	NA	NA	liquid	NA	NA
n-Butanol	NA	feedstock	r	air	NA	NA	gas	NA	NA
n-Butanol	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Sulfuric acid	NA	catalyst	r	water	NA	NA	liquid	NA	NA

Source: EPA 1981, Organic Chemical Producers Data Base.

+Emissions are routine (r).

REFERENCES

Faith, W.L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals. 3rd Ed. New York: John Wiley and Sons, Inc.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Technomic Publishing Company, Inc. Westport, Connecticut.

Herrick, E. C., J. A. King, R. P. Ouellette, and P. N. Cheremisinoff. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Kirk-Othmer. 1971. Encyclopedia of Chemical Technology. 3rd Ed. Volume 9. New York: John Wiley and Sons, Inc.

Morrison, R. T. and R. N. Boyd. 1973. Organic Chemistry, 3rd Ed. Boston, Massachusetts: Allyn and Bacon, Inc.

SRI International. 1981. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

U.S. EPA. 1981. Organic Chemicals Producers Data Base.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 7. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028b.

Wise, Hugh E. and Paul D. Fahrenthold. November 1981. Predicting Priority Pollutants from Petrochemical Processes. Environmental Science and Technology, 15, (11), pp. 1252-1304.

REFERENCES CONSULTED NOT CITED

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides, and Explosives Industries. U.S.Environmental Protecton Agency. Office of Solid Waste. Washington, D.C. EPA/530/SW-118C.

U.S. EPA. Office of Solid Waste, November 14, 1980. Background Document. Resource Conservation and Recovery Act, Subtitle C - Identification and Listing of Hazardous Waste, pp. 261.31 and 261.32. Listing of Hazardous Wastes (Finalization of May 19, 1980 Hazardous Waste List, p. 320-335).

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SECTION 12

HALOGENATION

12.0 INTRODUCTION

Halogenation is the process of reacting a hydrocarbon with a halogen gas. Direct chlorination to form chlorocarbons is the most widely used halogenation process. Table 12-1 lists major halogenation products and their 1980 manufacture.

Manufacture of halocarbons by direct halogenation involves three basic steps: (1) halogenation, (2) absorption, and (3) separation (Figure 12-1). Halogenation occurs in a reactor in the presence of a catalyst (catalytic reaction), heat (thermal reaction), or light (photochemical reaction). The reaction can take place at high temperature using light to promote the reaction. The reaction is dependent on the hydrocarbon used, catalyst used, hydrocarbon-halogen ratio, reaction temperature, pressure, and reactor space velocity (Khan et al. 1979, p. 8).

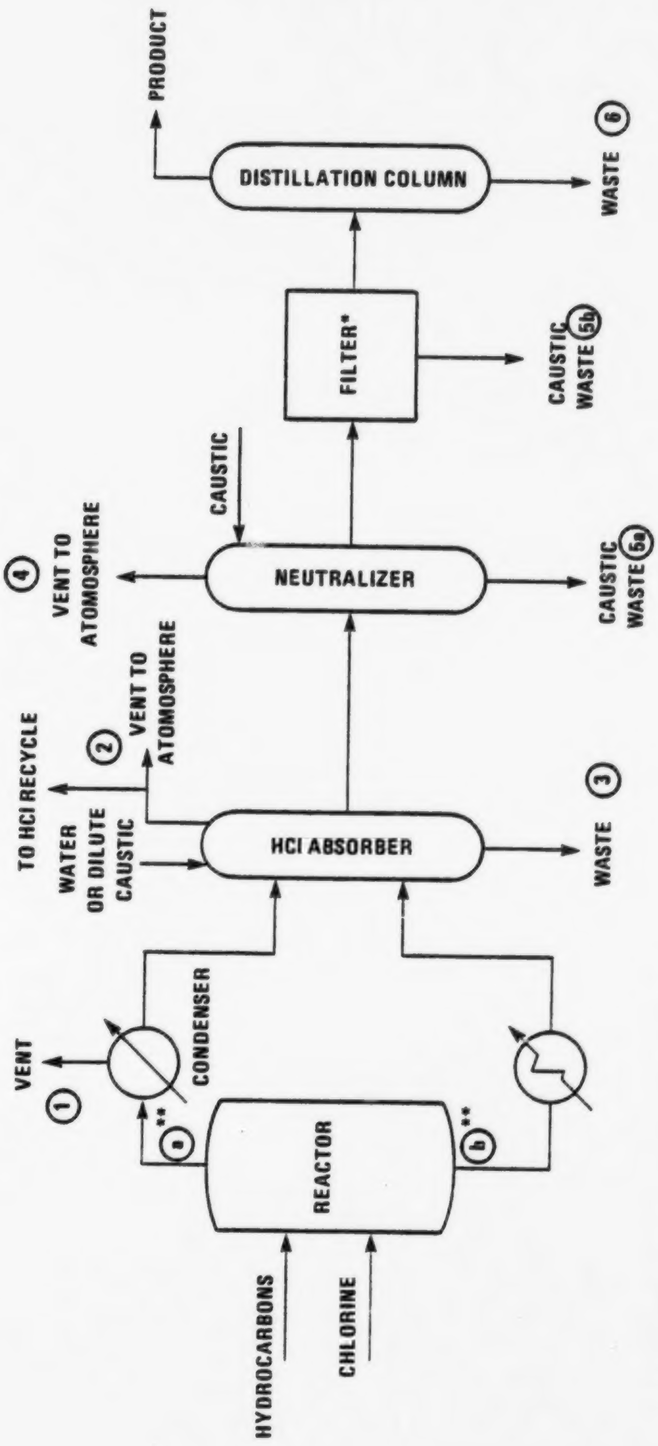
The reactor exit streams are sent to an absorber. The exit streams include crude product, by-products, unreacted raw materials, and catalyst, if used. In the absorption column, the unreacted raw materials are recovered, hydrohalogens (such as hydrogen chloride from chlorination) are recovered, and the products are sent to a separation and purification system.

Purification of the crude product is then carried out by separation. This can be done in one operation but usually involves several, including fractional distillation, neutralization, or scrubbing. After purification, the final halocarbon product is withdrawn and sent to storage for sale or use (Khan et al. 1979).

TABLE 12-1. HALOGENATION PRODUCTS AND THEIR MANUFACTURE IN 1980

Product	Amount (kkg)	Feedstock	Product	Amount	Feedstock
Benzyl Chloride	59,874	Toluene	Propylene oxide	533,425	Propylene, tert-butyl alcohol, and chlorine
Carbon Tetrachloride	72,574	Carbon disulfide			
	197,040	Methane	1,1,1-Trichloroethane	473,550	Ethylene or vinyl chloride
Chloreacetic acid	35,925	Acetic acid			
Chlorobenzene	228,610	Benzene	VCM	4,762,720	Ethylene-oxyhalogenation
Chloroform	186,880	Methanol		304,814	Ethylene
Dichlorobenzene	39,190	Benzene			
p-Dichlorobenzene	54,068	Benzene			
Ethylene dichloride	6,377,509	Ethylene			
Fluorocarbons	3,661,398	Carbon tetrachloride or methane Hydrofluoric acid			
Methyl chloride	272,155	Methanol			
Methylene chloride	174,179	Methanol			
	72,574	Methane			
	47,174	Methane and methanol			
Perchloroethylene	433,634	Ethylene dichloride or Acetylene			
Phosgene	687,646	Carbon monoxide			

Source: Herrick et al, 1979a and SRI International, 1981.



* USED IF CAUSTIC WASTE NOT SEPARATED IN NEUTRALIZER – EXCEPTION: VCM PROCESS

** FUGITIVE EMISSION POINTS

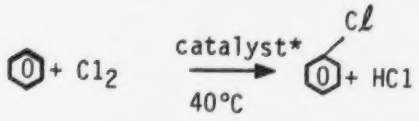
FIGURE 12–1: HALOGENATION OF HYDROCARBONS

SOURCE: KHAN ET AL, 1979

12.1 GENERAL CHEMISTRY

Halogenation involves introducing one or more halogen atoms into an organic compound. Direct halogenation, using a pure halogen, is a substitution reaction:

$$CH_4 + Cl_2 \xrightarrow{\text{light}} CH_3Cl + HCl$$



(*catalyst = $FeCl_3$, $AlCl_3$, Fuller's earth, or iron turnings)

The halogen undergoes homolysis, where cleavage of the halogen-halogen bond takes place in a symmetrical way, each atom retaining one electron of the pair, forming a free radical. The presence of free radicals sets up chain reactions:

$$Cl_2 \xrightarrow[\text{or light}]{\text{heat}} 2Cl\cdot$$

$$Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot$$

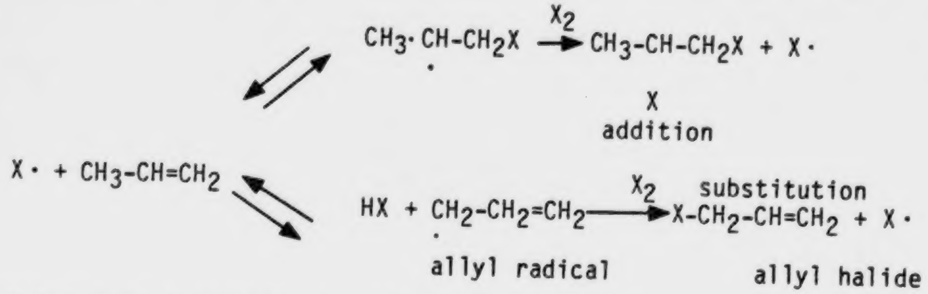
$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$$

$$CH_3\cdot + Cl \rightarrow CH_3Cl$$

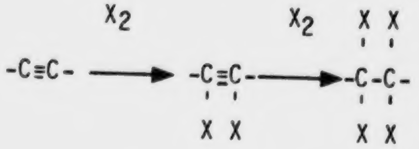
Chlorine is the most important halogen in the synthetic organic chemicals industry; however, fluorine, bromine, and iodine are also used. Their order of reactivity (tendency to substitute on a hydrocarbon), is as follows: $F_2 > Cl_2 > Br_2 > I_2$. After a halogenation reaction, one could have more excess organic with bromination than with chlorination.

With some hydrocarbons, side reactions, (other halogenation reactions) can occur resulting in multiple products. The orientation, or preferred reaction, is determined by the relative rates of the competing reactions. The less reactive a halogen is, the more selective it will be in its attack.

Another halogenation reaction is free radical addition. The following describes free halide radical addition (X·) versus substitution:

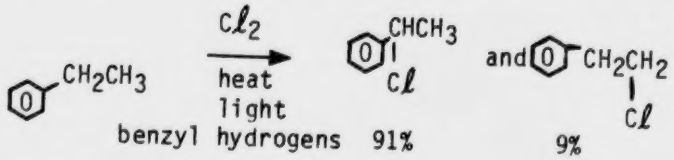

$X\cdot + CH_3\text{-}CH{=}CH_2$
$CH_3\cdot CH\text{-}CH_2X \xrightarrow{X_2} CH_3\text{-}CH\text{-}CH_2X + X\cdot$
X
addition
$HX + CH_2\text{-}CH_2{=}CH_2 \xrightarrow{X_2} X\text{-}CH_2\text{-}CH{=}CH_2 + X\cdot$
substitution
allyl radical
allyl halide

Halogen (X_2) addition to alkynes is as follows:

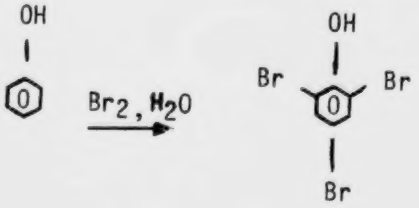


$$-C{\equiv}C- \xrightarrow{X_2} -\underset{X}{C}{=}\underset{X}{C}- \xrightarrow{X_2} -\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-$$

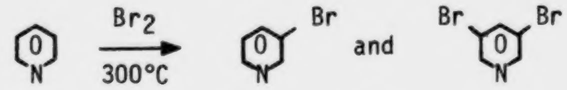
With alkylbenzenes, a halogen can attack the ring or side chain. One can control the site of attack chosen by reaction conditions because alkanes halogenation requires heat or light, and benzene halogenation requires an acid catalyst. Whereas an atom attacks a side chain, an ion from an acid catalyst attacks a ring. Normally, then, with direct halogenation of an alkylbenzene, a benzyl hydrogen, one on the side chain adjacent to the ring, will be attacked:



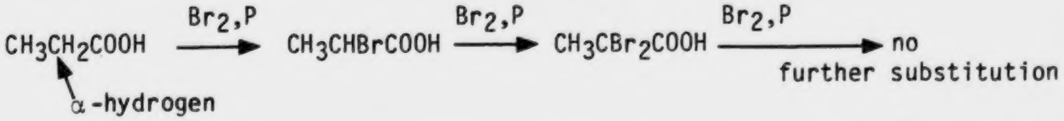
Other ring reactions have various site preferencs. Halogenation of phenols results in ortho- and para-substitution:



The reaction of a halogen with pyridine results in meta-substitution:



The reaction of a halogen with an aliphatic acid involves α-halogenation in the presence of phosphorus; only the α-hydrogens (on the carbon adjacent to the acid group) are replaced by the halogen. This is known as the Hell-Volhard-Zelinsky reaction and is described as follows:



$$CH_3\underset{\uparrow\,\alpha\text{-hydrogen}}{CH_2}COOH \xrightarrow{Br_2,P} CH_3CHBrCOOH \xrightarrow{Br_2,P} CH_3CBr_2COOH \xrightarrow{Br_2,P} \text{no further substitution}$$

Data for this section can be found in Morrison and Boyd (1973).

12.2 DESCRIPTION OF DISCHARGES

Among the discharges, fugitive and routine, the feedstock hydrocarbons and chlorine are usually present. The product halocarbon is emitted at most discharge points, along with heavier and lighter halogenated hydrocarbon by-products. The heavies produced are mostly drawn off in the final wastewater of the distillation column(s). Hydrogen chloride, which is generated during halogenation, is among the emissions from the HCl scrubber. If a neutralizer is employed in the process, excess sodium hydroxide and sodium chloride by-product are exited in the bottoms of the neutralizer column or drawn off from a filter. Tars and carbon solids are present in the final distillation column bottoms waste, and if a catalyst is used, catalyst fines such as mercuric chloride or antimony trichloride will also be present.

12.3 DESCRIPTION OF AN EXAMPLE PRODUCTION PROCESS: MANUFACTURE OF CHLOROMETHANES - THE DIRECT CHLORINATION OF METHANE

This description of the manufacture of chloromethanes by the direct chlorination of methane consists of seven major steps: (1) first chlorination (reactor #1), (2) "lights" purification (from the absorber through the drying column), (3) "lights" separation (methyl chloride and methylene dichloride columns), (4) second chlorination (reactor #2), (5) chloroform purification (intermediate and chloroform columns), (6) final chlorination (reactor #3), and (7) carbon tetrachloride purification. Figure 12-2 illustrates this process. For each part, the description highlights the emissions associated with that step of the process.

12.3.1 Chlorination Reaction

Methane and chlorine, in a molar ratio of approximately 2 to 1, are mixed and preheated. They are then fed to a reactor (Figure 12-2) fitted with mercury arc lamps. The reaction occurs at a temperature of 350 to 370°C and approximately atmospheric pressure, with residence time controlled to maintain desired temperature. Methyl chloride is the primary chlorination product from this reactor, about 58.5% of the total chloromethanes produced; methylene dichloride makes up 29.3%; chloroform makes up 9.7%; and carbon tetrachloride makes up 2.3% (Faith et al. 1965, p. 508).

12.3.1.1 Emissions

Fugitive emissions from feed valves to and from the reactor may include chlorine gas, methane, chloromethanes, and hydrogen chloride (Khan et al. 1979).

12.3.2 Purification

From the reactor, the mixture enters an absorber in which the effluent gases are scrubbed with a mixture of chloroform and carbon tetrachloride which is fed from stripper, which is the next column. Unreacted methane and hydrogen chloride, present in the effluent gases from the reactor, are not absorbed and are consequently separated from the mixture and removed in the overhead stream, where the two are separated in a water absorber and where the methane is recycled. The absorbed chloromethanes are fed to a stripper where methyl chloride and some methylene dichloride pass overhead. Part of the bottoms, as previously mentioned, are recycled as absorbent in the first absorber; the remainder is sent to a second reactor for further product separation and purification. The overhead stream is further purified in a hydrogen chloride scrubber, where hot water

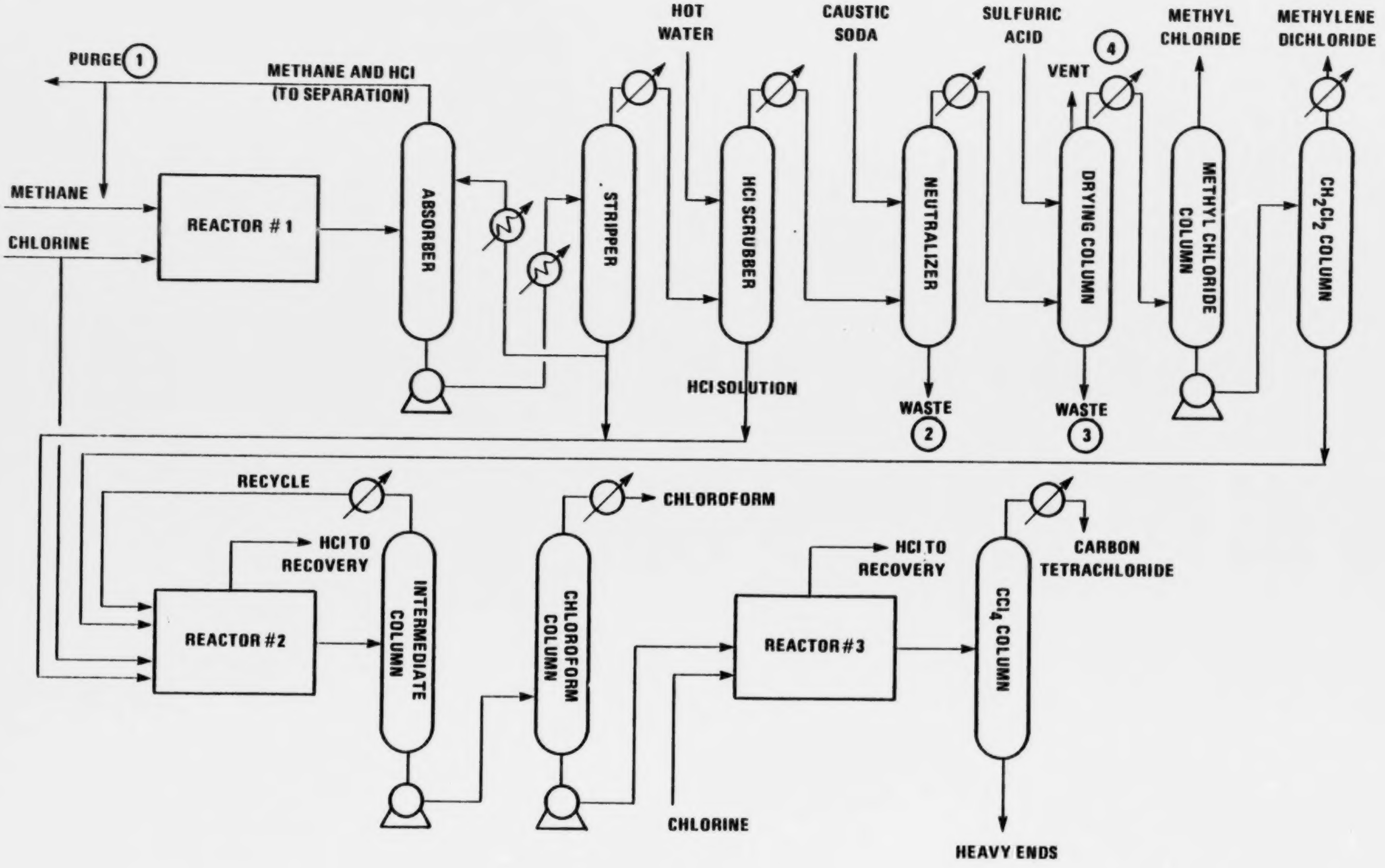


FIGURE 12–2: CHLOREMETHANES MANUFACTURE

SOURCE: FAITH, KEYES AND CLARK, 1965

washes the HCl from the mixture and the chloromethanes exit as overhead to a neutralizer. In the neutralizing column, remaining HCl is neutralized with a caustic soda solution and the resulting salt exits through the bottom in wastewater. The chloromethanes are again removed as overhead and enter a drying column where a strong sulfuric acid wash is introduced to dry the mixture. After this final purification step, the chloromethanes, methyl chloride and methylene dichloride, are ready to be separated (Faith et al. 1965, p. 509).

12.3.2.1 Emissions

The neutralizer and drying column bottoms are the major wastewater sources. They contain chloromethanes that get washed down with caustic soda in the neutralizer and sulfuric acid in the drying column.

Air emissions from the purification section include the purge gas to air from the methane recycle system and leaks from valves, pumps, compressors, seals, valve stems, and flanges (Khan et al. 1979, p. 50).

12.3.3 Separation

The first chloromethane separation produces methyl chloride and methylene dichloride, the "lights" of the chloemethane mixture. After purification, the lights enter a fractional distillation column, where methyl chloride evaporates and exits the column as overhead gas in final product form. The bottoms of this column enter a second fractional distillation column in which methylene dichloride vaporizes and exits as overhead gas through a condenser where it is cooled to its final product form of a liquid. The "heavies," containing the chloromethanes, chloroform and carbon tetrachloride, exit the column as bottoms to a second reactor, where further chlorination occurs (Faith et al. 1965, p. 509).

12.3.3.1 Emissions

Fugitive emissions may occur at valves, pumps, flanges, etc., (Khan et al. 1979, p. 51).

12.3.4 Second Chlorination

The bottoms from the methylene dichloride column and part of that from the stripping column are fed to a secondary reactor, where more chlorine is added. Again, a photochemical chlorination reaction is carried out, but this time in the liquid phase. Hydrogen chloride is vented from the reactor, and the reaction products are sent to a purification system. The major product is chloroform and some carbon tetrachloride, with some unreacted methyl chloride and methylene dichloride (lights) (Faith et al. 1965).

12.3.4.1 Emissions

Fugitive emissions may occur from valves, pumps, fittings, etc. (Khan et al. 1979).

12.3.4 Chloroform Purification

The mixture from the second reactor enters an intermediate column, where the lights (methyl chloride and methylene dichloride) exit as overhead gases, are condensed, and are recycled to the reactor for further chlorination. The bottoms, containing mostly chloroform, enter a distillation column, and the chloroform exits as overhead gas and is condensed to a final form of a water-white liquid. The bottoms are sent to a third chlorinator (Faith et al. 1979).

12.3.5 Emissions

Fugitive emissions may occur from valves, pumps, compressors, etc., (Khan et al. 1979).

12.3.6 Final Chlorination

In this reactor, the remaining liquid "heavies" are treated with chlorine in the presence of mercury lamps to form carbon tetrachloride. Again HCl is vented from the reactor, and this reaction mixture enters a final distillation (Faith et al. 1965).

12.3.6.1 Emissions

Fugitive emissions may occur from valves pumps, etc. (Khan et al. 1979).

12.3.7 Carbon Tetrachloride Separation and Purification

The final product of methane chlorination is carbon tetrachloride. This is separated from any remaining heavy ends in a distillation column. After the gaseous carbon tetrachloride exits the column as overhead, it is condensed to its heavy liquid final form. The heavy ends exit as bottoms to wastewater. (Faith et al. 1965, p. 509).

12.3.7.1 Emissions

Heavy ends from distillation column bottoms go to wastewater. Fugitive emissions may also escape from valves, pumps, fittings, etc. (Khan et al. 1979).

12.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the following manufacturing processes:

i) Chlorobenzene (Table 12-2)
ii) Vinyl chloride monomer (Table 12-3)
iii) Allyl chloride (Table 12-4)
iv) Chloroprene (Table 12-5)
v) Trichloroethylene (Table 12-6)
vi) Perchloroethylene (Table 12-7)
vii) Ethylene dichloride (Table 12-8)
viii) Chlorotoluene (Table 12-9)
ix) Chloromethanes (Table 12-10)

The locations of emissions sources for Tables 12-2 through 12-9 are found by consulting Figure 12-1, and for Table 12-10 are found in Figure 12-2. Releases are characterized as either routine (r) or accidental (a), controlled or uncontrolled. Catalytic waste amounts were not available for all the chemicals studied. Chlorine gas emissions were found for ethylene dichloride production only.

Table 12-2 CHARACTERIZATION OF EMISSIONS FROM THE CHLOROBENZENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
HCl	HCl scrubber - 2	by-product	r	air	1.4^{1}	NA	gas	NA	NA
Monochlorobenzene	HCl scrubber - 2	product	r	air	0.03^{2}	NA	gas	NA	NA
	1st column wash - 6a		r	water	0.88^{1}	NA	liquid	NA	NA
	2nd column waste-stream - 6b		r	land	$<1.0^{1}$	NA	liquid	NA	NA
Dichlorobenzene	HCl scrubber - 2	product	r	air	$<0.001^{2}$	NA	gas	NA	NA
	1st column wash - 6a		r	water	3.7^{1}	NA	liquid	NA	NA
	2nd column waste-stream - 6b		r	land	0.1^{1}	NA	liquid	NA	NA
Other hydrocarbons	HCl scrubber - 2	by-product	r	air	$<0.001^{2}$	NA	gas	NA	NA
Polychlorinated aromatic resins	2nd column waste-stream - 6b	by-product	r	land	44^{1}	NA	liquid	NA	NA
Benzene	HCl scrubber - 2	feedstock	r	air	0.002^{2}	NA	gas		
	caustic scrubber - 4		r	air	0.52^{3}	5.7^{3}**	gas	carbon adsorption	0.0067^{4}**
	dist. col. (1) - 6a		r	air	0.32^{3}	3.5^{3}**	gas	carbon adsorption	0.0042^{4}**
	dist. col. (2) - 6b		r	air	0.04^{3}	0.48^{3}**	gas	vent to process	0^{4}**
	pump seals, valves, compressor seals, flanges, and drains		a	air	0.58^{3}	6.4^{3}**	gas	detection and repairs of major leaks	0.16^{4}**
Other VOC	caustic scrubber - 4	by-products	r	air	0.09^{3}	1.0^{3}**	gas	carbon adsorption	0.0012^{4}**
	dist. col. 1 - 6a		r	air	0.03^{3}	0.3^{3}**	gas	carbon adsorption	0.0003^{4}**
	vacuum system vent		r	air	0.03^{3}	0.46^{3}**	gas	carbon adsorption	0.0003^{4}**
	p-DCB crystallizer		r	air	0.46^{3}	0.183**	gas	none	0.006^{4}**
	p-DCB crystal processing		r	air	0.016^{3}	0.92^{3}**	gas	carbon adsorption	0.001^{4}**
	pump seals, valves, compressor seals, flanges, and drains		a	air	1.39^{3}	15.2^{3}**	gas	detection & repair of major leak	0.42^{4}**

[1] Gruber, 1975, p. 5-15.

[2] Khan et al, 1979, p. 53.

[3] White, 1981. Vol. 6, Report 3, p. IV-3.

[4] Ibid, p. V-2.

+Denotes that a release is routine (r) or accidental (a)

**Based on annual plant production of 96,000 kkg chlorobenzenes

TABLE 12-3 CHARACTERIZATION OF EMISSIONS FROM THE VINYL CHLORIDE MONOMER MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of† Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Ethylene	neutralizer - 5a	product	r	Water	4.35^1	NA	Liquid	NA	NA
	2nd still (vent) condenser - 6b*		r	Air	12^{1*}	NA	Gas	NA	NA
	filter - 5b		r	Land	0.5^{1*}	NA	Liquid	NA	NA
	1st still - 6a		r	Land	2.4^{1*}	NA	Liquid	NA	NA
	3rd still - 6c		r	Land	0.8^1	NA	Liquid	NA	NA
Sodium hydroxide	neutralizer - 5a	additive	r	Water	0.98^{1*}	NA	Liquid (in solution)	NA	NA
	filter - 5b		r	Land	trace^{1*}	NA		NA	NA
Sodium chloride	neutralizer - 5a	by-product	r	Water	0.33^{1*}	NA	Liquid (in solution)	NA	NA
Vinyl chloride	neutralizer - 5a	product	r	Water	0.98^{1*}	NA	Liquid	NA	NA
Methyl chloride	neutralizer - 5a	by-product	r	Water	0.85^{1*}	NA	Liquid	NA	NA
Ethyl chloride	neutralizer - 5a	by-product	r	Water	0.85^{1*}	NA	Liquid	NA	NA
Tars	filter - 5b	by-product	r	Land	trace^{1*}	NA	Solid	NA	NA
	1st still - 6a		r	Land	trace^{1*}	NA	Solid	NA	NA
	3rd still - 6c		r	Land	0.05^{1*}	NA	Solid	NA	NA
Carbon solids	filter - 5b	by-product	r	Land	0.08^{1*}	NA	Solid	NA	NA
	3rd still - 6c		r	Land	0.2^{1*}	NA	Solid	NA	NA
Methane	2nd still condenser vent - 6b	by-product	r	Air	4.9^{1*}	NA	Gas	NA	NA
1,1,1-Trichloroethane	1st still - 6a	by-product	r	Land	4.0^{1*}	NA	Liquid	NA	NA
Tetrachloroethane	1st still - 6a	by-product	r	Land	4.0^{1*}	NA	Liquid	NA	NA

TABLE 12-3 CHARACTERIZATION OF EMISSIONS FROM THE VINYL CHLORIDE MONOMER MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Heavy ends	3rd still - 6c	by-product	r	Land	3.7^{1*}	NA	NA	NA	NA
Mercuric chloride	3rd still - 6c	catalyst	r	Land	0.005^{1*}	NA	Solid	NA	NA

[1] Gruber, 1975, p. 5-35 & 5-36.

+Denotes that a release is routine (r) or accidental (a).

*Three consecutive distillation columns used; 2nd still has overhead waste.

**Based on "typical plant size" of 136,000 kkg/yr.

TABLE 12-4 CHARACTERIZATION OF EMISSIONS FROM THE ALLYL CHLORIDE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Propylene	absorber - 2	feedstock	r	Air	13.5[1]	NA	gas	NA	NA
Ethyl chloride	absorber - 2	by-product	r	Air	13.5[1]	NA	gas	NA	NA

---

[1] Hadley et al. 1975, p. 136 - no production capacity given

TABLE 12-5 CHARACTERIZATION OF EMISSIONS FROM THE CHLOROPRENE MANUFACTURING PROCESS

Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Uncontrolled Emissions		Form	Controlled Emissions	
					Quantity kg/kkg Product	Rate kg/hr		Control Technology	Quantity kg/kkg Product
Sodium chloride	HCl absorber - 3	by-product	r	Water	500[1]	NA	liquid (in solution)	NA	NA
Sodium hydroxide	HCl absorber - 3	additive	r	Water	125[1]	NA	liquid (in solution)	NA	NA
Organic by-products	HCl absorber - 3 reactor - 1	by-product	r	Water Air	NA NA	NA NA	liquid gas	NA NA	NA NA
HCl	reactor - 1	by-product	r	Air	NA	NA	gas	NA	NA

[1] Hedley et al. 1975, p. 263 - no production capacity given.

+Denotes that a release is routine (r) or accidental (a).

TABLE 12-6 CHARACTERIZATION OF EMISSIONS FROM THE TRICHLOROETHYLENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Ethane	reactor condenser - 1	by-product	r	Air	1.25[1]	NA	gas	NA	NA
Methane	reactor condenser - 1	by-product	r	Air	1.25[1]	NA	gas	NA	NA
Tetrachloroethane	reactor condenser - 1	by-product	r	Air	0.50[1]	NA	gas	NA	NA
	absorber - 2		r	Air	0.05[1]	NA	gas	NA	NA
HCl	absorber - 2	by-product	r	Air	0.1[1]	NA	gas	NA	NA
Trichloroethylene	absorber - 2	product	r	Air	0.35[1]	NA	gas	NA	NA
Perchloroethylene	absorber - 2	by-product	r	Air	0.1[1]	NA	gas	NA	NA
Chloromethanes, chlorinated hydrocarbons	process effluents	by-product	r	water	NA[2]	NA	liquid	NA	NA

---

[1] Hedley et al, 1975 p. 302 - Based on 18,144 kkg/yr capacity.

[2] Wise and Fahrenthold. 1981. Taken from Table 3. Pollutant concentrations are at least 0.5 ppm. Feedstock includes 1,2-dichloroethane.

+Denotes that a release is routine (r) or accidental (a).

TABLE 12-7 CHARACTERIZATION OF EMISSIONS FROM THE PERCHLOROETHYLENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Ethane	1st vent reactor condenser - 1	by-product	r	Air	1.135^1	NA	gas	NA	NA
Methane	1st vent reactor condenser - 1	by-product	r	Air	1.135^1	NA	gas	NA	NA
Antimony trichloride	1st vent reactor condenser - 1	catalyst	r	Air	0.001^2	NA	gas	NA	NA
Tetrachloro-ethane	1st vent reactor condenser - 1	by-product	r	Air	0.453^1	NA	gas	NA	NA
	HCl absorber - 2		r	Air	0.453^1	NA	gas	NA	NA
Hydrogen-chloride	HCl absorber - 2	by-product	r	Air	0.9^1	NA	gas	NA	NA
Trichloro-ethylene	HCl absorber - 2	by-product	r	Air	0.3175^1	NA	gas	NA	NA
	2nd reactor - 7**		r	Air	2.8^1	NA	gas	NA	NA
Tetrachloro-ethylene	HCl absorber - 2	by-product	r	Air	0.9^1	NA	gas	NA	NA
Pentachloro-ethane	2nd reactor - 7	by-product	r	Air	0.3^1	NA	gas	NA	NA
Dichloro-ethane	2nd reactor - 7	by-product	r	Air	2.35^1	NA	gas	NA	NA
Chlorinated solvents	2nd neutralizer - 11a	by-product	r	Water	trace^1	NA	liquid	NA	NA
Calcium	2nd neutralizer - 11a	by-product	r	Water	240.5^1	NA	solid	NA	NA

TABLE 12-7 CHARACTERIZATION OF EMISSIONS FROM THE PERCHLOROETHYLENE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Calcium chloride	2nd neutralizer - 11a	by-product	r	Water	344.5[1]	NA	liquid (in solution)	NA	NA
Hexachlorobutadiene	dist. col.'s - 6 & 12	by-product	r	Land	230[1]	NA	liquid	NA	Na
Chlorobenzenes	dist. col.'s - 6 &12	by-product	r	Land	10[1]	NA	liquid	NA	NA
Chloroethanes	dist. col.'s - 6 & 12	by-product	r	Land	10[1]	NA	liquid	NA	NA
Chlorobutadienes	dist. col.'s - 6 & 12	by-product	r	Land	10[1]	NA	liquid	NA	NA
Tars & Residues	dist. col.'s - 6 & 12	by-product	r	Land	20[1]	NA	solid	NA	NA
Other Material	dist. col.'s - 6 & 12	by-product	r	Land	10[1]	NA	NA	NA	NA

[1] Gruber, 1975. p. 5-5. Based on "typical plant size" of 32,000 to 45,000 kkg/yr.

[2] Gruber, 1975. p. 5-3. Based on "typical plant size" of 32,000 to 45,000 kkg/yr.

+ Indicates if emission was routine (r) or fugitive accidental (a).

**7-12 are 2nd reaction equipment points of emission (correspond with 1-6).

TABLE 12-8 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE DICHLORIDE MANUFACTURING PROCESS

Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg Product	Uncontrolled Emissions Rate kg/hr	Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg Product
Ethane	reactor condenser - 1	by-product	r	air	3^{1**}	NA	gas	NA	NA
Ethylene dichloride	reactor condenser - 1	product	r	air	1.08^{2}-7.5^{1**}	49.1^{2}	gas	Thermal oxidizer	0.00108^{4}
	HCl absorber (3)		r	water	2.5^{1**}	NA	liquid	NA	NA
	HCl vent - 2		r	Air	2.2^{3}	NA	gas	NA	NA
	HCl bottoms - 3		r	water	1.8^{3}	NA	liquid	NA	NA
	caustic storage		r	water	0.15***	NA	liquid	NA	NA
	filter effluent - 5b		r	water	0.3^{1***}	NA	liquid	NA	NA
	column bottoms - 6		r	land	1.45^{1***}	NA	liquid	NA	NA
	pump seals, valves, compressor seals, flanges & drains		a	air	0.265^{2}	12.1^{2}	gas	Detection & Correction of Major Leaks	0.0743^{4}
Methane	reactor condenser - 1	by-product	r	air	3^{1**}	NA	gas	NA	NA
Chlorine	reactor condenser - 1	feedstock	r	air	0.0005^{1**}	NA	gas	NA	NA
	reactor overhead & bottoms - 1a&1b		a	air & water	0.4^{3}	NA	gas & liquid	NA	NA
	HCl absorber-3		r	water	0.875^{1**}	NA	liquid (in solution)	NA	NA
Hydrogen chloride	reactor condenser	by-product	r	air	0.0005^{1**}	NA	gas	NA	NA
	reactor overhead & bottoms - 1a & 1b		a	air & water	0.4^{3}	NA	gas & liquid	NA	NA
	HCl absorber - 3		r	water	0.4^{3} 3.8^{1**}	NA	liquid	NA	NA
Vinyl chloride	HCl abosrber - 3	by-product	r	water	0.6^{1**}	NA	liquid	NA	NA
Methyl chloride	HCl absorber - 3	by-product	r	water	0.05^{1**}	NA	liquid	NA	NA
Ethyl chloride	HCl absorber - 3	by-product	r	water	0.05^{1**}	NA	liquid	NA	NA

TABLE 12-8 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE DICHLORIDE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Tars	filter effluent - 5b	by-product	r	land	trace[1][**]	NA	solid	NA	NA
	dist. col. bottoms - 6		r	land	trace[***]	NA	solid	NA	NA
Carbon solids	filter effluent - 5b	by-product	r	land	0.05[1][***]	NA	solid	NA	NA
1,1,2-Trichroethane	dist. col. bottoms - 6	by-product	r	land	2.45[1][***]	NA	liquid	NA	NA
	reactor overhead and bottoms - 1a & 1b		r	water & air	10.1[3]	NA	gas & liquid	NA	NA
Tetrachloroethane	dist. col. bottoms - 6	by-product	r	land	2.45[1][***]	NA	liquid	NA	NA
Other VOC	reactor vent - 1	by-product	r	air	1.76[2]	80.9[2]	gas	Thermal Oxidizer	0.00176
	pump seals, valves, compressor seals, flanges & drains		a	air	0.268[2][*]	12.2[2][*]	gas	Detection & Correction of Major Leaks	0.00747
Mercuric hydroxide	filter effluent - 5b	NA	r	land	0.0035[1][***]	NA	solid	NA	NA
Sodium hydroxide	caustic storage	caustic	r	water	0.6[1][***]	NA	liquid	NA	NA
	filter effluent	caustic	r	water	trace[1][***]	NA	liquid	NA	NA
Sodium chloride	caustic storage	by-product	r	water	0.2[1][***]	NA	liquid	NA	NA

---

[1] Hedley et al, 1975. p. 194-5.

[2] White, 1981. Vol. 8, report 1, p. IV-3.

[3] Khan et al, 1979. p. 19 - no plant capacity given.

[4] White, 1981. Vol. 8, report 1, p. V-2.

+Denotes that a release is routine (r) or accidental (a).

[*] Based on annual plant production of 215,000 kkg.

[**] Based on 24,312 kkg/yr capacity.

[***] Based on 72,575 kkg/yr capacity.

TABLE 12-9 CHARACTERIZATION OF EMISSIONS FROM THE CHLOROTOLUENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location Refer to Figure 12-1	Source	Type of+ Release	Receiving Medium	Quantity kg/kkg Product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg Product
Benzyl chloride	dist. col. - 6	by-products	r	Land	0.5[1]	NA	liquid	liquid	NA
Benza-trichloride	dist. col. - 6	by-products	r	Land	0.5[1]	NA	liquid	liquid	NA

[1] Gruber, 1975, p. 5-50.

*Based on "typical process facility sizes" of 10,000 to 15,000 kkg/year.

+Denotes that a release is routine (r) or accidental (a).

TABLE 12-10 CHARACTERIZATION OF EMISSIONS FROM THE CHLOROMETHANES MANUFACTURING PROCESS

Pollutant	Location Refer to Figure 12-2	Source	Type of+ Release	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg Product	Rate kg/hr	Form	Controlled Emissions Control Technology	Quantity kg/kkg Product
Methane	CH_4 recycle (purge) -1	feedstock	r	Air	1^1	NA	gas	NA	NA
Methyl-chloride	CH_4 recycle - 1	product	r	Air	13^1	NA	gas	NA	NA
	Neutralizer bottoms - 2		r	Water	0.02^1	NA	liquid	NA	NA
	Dehydrator bottoms - 3		r	Water	0.03^1	NA	liquid	NA	NA
Methylene chloride	CH_4 recycle - 1	product	r	Air	2^1	NA	gas	NA	NA
	Neutralizer bottoms - 2		r	Water	0.02^1	NA	liquid	NA	NA
	Dehydrator bottoms - 3		r	Water	0.03^1	NA	liquid	NA	NA
Chloroform	CH_4 recycle - 1	product	r	Air	1^1	NA	gas	NA	NA
	Neutralizer bottoms - 2		r	Water	0.02^1	NA	liquid	NA	NA
	Dehydrator bottoms - 3		r	Water	0.03^1	NA	liquid	NA	NA
Carbon	CH_4 recycle - 1	product	r	Air	1^1	NA	gas	NA	NA
	Neutralizer(b) - 2		r	Water	0.02^1	NA	liquid	NA	NA
	Dehydrator(b) - 3		r	Water	0.03^1	NA	liquid	NA	NA
Perchloethylene	Neutralizer(b) - 2	by-product	r	Water	0.02^2	NA	liquid	NA	NA
	Dehydrator(b) - 3		r	Water	0.03^2	NA	liquid	NA	Na
VOC Emissions**	CH_4 recycle (purge) - 1	products	r	Air	2.10^2	48.0^{2**}	gas	Absorber	0.22
	Dehydrator (OH) - 4		r	Air	0.052^2	14.5^{2**}	gas	None	0.052
	Pump seals, valves, compressor seals, flanges, and drains		a	Air	1.74^2	39.7^{2**}	gas	Detection & Correction of Major Leaks	0.057

*[1] Gruber, 1975, p. 5-52. For methylene chloride, manufacture only at "typical production facility size" of 15,000 kkg/year.
**[2] White, 1981. Vol. 8., Report 5, p. IV-3. Includes all chloromethanes at annual plant production of 200,000 kkg.
**[3] Ibid, p. V-3.

+Denotes that a release is routine (r) or accidental (a).

(OH) = overhead
(b) = bottoms

REFERENCES

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals. 3rd Ed. New York, New York: John E. Wiley and Sons, Inc.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. For Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitg, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Technomic Publishing Company, Inc. Westport, Connecticut.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science.

Khan, Z. S., and T. W. Hughes. Monsanto Research Corporation. 1979. Source Assessment: Chlorinated Hydrocarbons Manufacture. For Environmental Protection Agency. Industrial Environmental Research Laboratory. Research Triangle Park, North Carolina. EPA/600/2-79-019G.

Morrison, R. T., and R. N. Boyd. 1978. Organic Chemistry, 3rd Ed. Boston, Massachusetts: Allyn and Bacon, Inc.

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 8. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028c.

Wise, Hugh E. Jr. and Paul D. Fahrenthold. November 1981. Priority Pollutants from Petrochemical Processes. Environmental Science and Technology, 15, (11), pp. 1292-1304.

SECTION 13 - HYDRODEALKYLATION

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SECTION 13

HYDRODEALKYLATION

13.0 INTRODUCTION

Hydrodealkylation is the process by which a methyl or larger alkyl groups is removed from hydrocarbon molecules and replaced by hydrogen atoms (Herrick 1980). Benzene and napthalene are produced by this process. USITC (1979) reported that 5351389.3 kkg of benzene and 74102 kkg of napthalene were produced from petroleum in 1979. Versar (1979) reported that 28% of the total petroleum based benzene was produced by toluene hydrodealkylation in 1976. Assuming this percentage for 1979, total benzene production by hydrodealkylation is 1,498,400 kkg. Table 13-1 presents the chemicals produced, other processes required, and the feedstocks required for the hydrodealkylation process. The principal feedstock used is toluene (Kirk-Othmer 1978). The commercial processes used for hydrodealkylation are either catalytic or thermal. The frequency of the use of these processes is about equal, and the process steps are similar (Kirk-Othmer 1978).

Catalytic processes include the Hydeal (UOP) and the Detol (Houdry). The thermal processes most widely used are HDA (ARCO and Hydrocarbon Research Institute) and THD (Gulf). For catalytic production, the catalyst used is usually chromium-on-alumina or platinum-on-alumina. Toluene is heated to 590-650° C for catalytic hydrodealkyelation and as high as 760° C in the thermal process (Kirk-Othmer 1978). Figure 13-1 is a flow diagram of a typical hydrodealkylation process. Table 13-2 lists present methods and process conditions for the toluene hydrodealkylation process to produce benzene.

Benzene is included in the Environmental Protection Agency's 129 priority pollutants. It is toxic to man and aquatic organisms. It is mutagenic and probably carcinogenic in man and teratogenic in mice (Versar 1980). The toxicity of benzene has prohibited its use as a solvent except in unusual circumstances such as the paint and surface coating industry.

TABLE 13-1. ORGANIC CHEMICALS MANUFACTURED BY HYDRODEALKYLATION

Other Processes Required	Product	Feedstock	Amount kkg for 1979
None	Benzene Light hydrocarbon	Aromatic mixtures Hydrogen	NA
None	Benzene	Coke oven light oil	NA
None	Benzene	Toluene	1,498,400
None	Benzene	Xylenes (mixed)	NA
None	Napthalene	Alkylnapthalenes	74,102

Source: Herrick, et al. 1979a.

FIGURE 13-1. A TYPICAL HYDRODEALKYLATION PROCESS

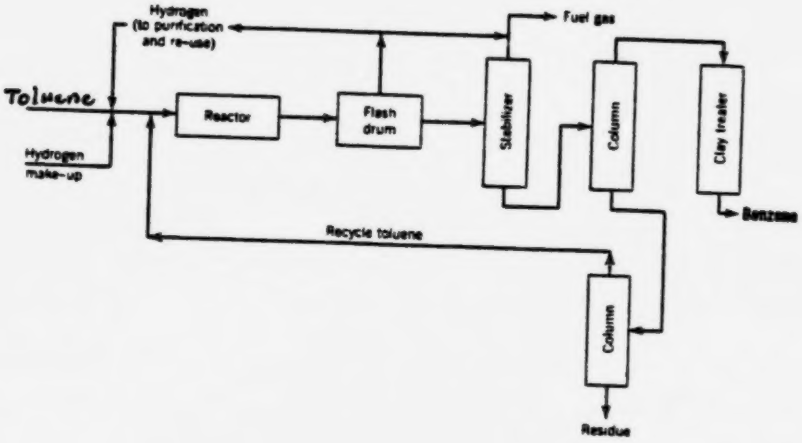


TABLE 13-2. TOLUENE HYDRODEALKYLATION METHODS USED TO PRODUCE BENZENE

Method	Process	Method Conditions	Yields
Catalytic	Hydeal (UOP) Detol (Houdry)	Temperature 540-650° C Pressure 500-1200 PSIG Catalyst unreported	70-80% per pass; ultimate yields of 95-98%
Thermal	HDA (ARCO) THD (Gulf)	Temperature 540-760° C Pressure 500-1200 PSIG	70-80% per pass; ultimate yields of 95-98%

Source: Adapted from Kirk-Othmer, 1978, and Parsons et al. 1977.

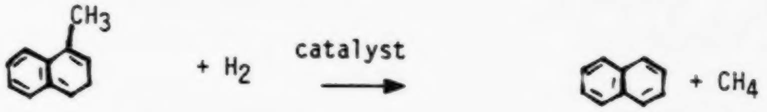
13.1 GENERAL CHEMISTRY

When dealkylation occurs with a hydrogen replacing the alkyl group, the method is called hydrodealkylation. Benzene is produced from toluene by catalytic or thermal dealkylation. Toluene reacts with hydrogen to yield benzene and methane gas, as shown in the following reaction:

$$C_6H_5CH_3 + H_2 \longrightarrow C_6H_6 + CH_4$$

A list of feedstocks and the chemical reactions in the production of benzene by dealkylation methods is presented in Table 13-3.

Napthalene is produced from the dealkylation of feed materials rich in alkyl napthalenes in the presence of hydrogen. It is produced by the Hydeal process of UOP. In addition to naphthalene, the process yields fuel gas, a light naptha high in benzene, and heavy components used for fuel. A typical reaction for the formation of napthalene from methylnapthalene is the following:



13.2 DESCRIPTION OF DISCHARGES

Descriptions of discharges are provided for the two major alkylation manufacturing processes; i.e., benzene and napthlene.

13.2.1 Benzene

Waste streams originate from periodic catalyst regeneration, fugitive emissions from valves and pump seals, discarding spent clay, operating power generation and cooling water systems, gas compressors, and process heaters. Catalyst regeneration in the Detol Process involves occasional burning of coke deposits in a preheated inert gas with controlled quantities of air. Descriptions of the Hydeal process indicate that about 1% of aromatics in the feed may be converted to heavy aromatics such as

TABLE 13-3. FEEDSTOCK AND CHEMICAL REACTIONS FOR THE DEALKYLATION METHOD OF BENZENE PRODUCTION

Feedstock	Frequency of Use	Chemical Reaction
92-95% Toluene	Usual feedstock	Demethylation
85-90% Toluene	Less frequently used	Demethylation, Dealkylation
Longer chain alkyl chains: heavy catalytic reformates, catalytic oils	Much less than the first two feedstocks	Combination of demethylation and dealkylation

Source: JRB, 1980.

biphenyl, methyl biphenyls, and flourene through condensation of aromatic nuclei. These heavy aromatics will most likely be found in the waste stream.

13.2.2 Napthalene

Fugitive emissions of hydrocarbons to the air are expected from distillation units, vents, pumps, seals, and flanges. For processes which use catalysts, catalyst decoking operations can be expected to release particulates, sulfur oxides, and carbon monoxides to the atmosphere. Atmospheric emissions are also expected from process heaters and cooling water treatment.

Solid waste consists of spent catalyst and acid treated clay used in purification. The usual method of disposal is by landfill. It is possible that some of the sorbed materials are toxic and could be mobilized into the environment by leaching of the landfill.

13.3 A PRODUCTION PROCESS: MANUFACTURE OF BENZENE BY HYDRODEALKYLATION

Hydrodealkylation consists of the following basic steps:

a. dealkylation
b. stabilization
c. distillation

Figure 13-2 is a detailed flow diagram for the hydrodealkylation process.

13.3.1 Dealkylation

Reactor feed (toluene), compressed recycled toluene, and hydrogen are preheated in heat exchanger(s) with recycle process streams and then passed through a fired heater. Dealkylation is achieved in the presence of hydrogen in a thermal or catalytic reactor. The reactor effluent is cooled using a waste heat boiler in some process designs and in others by exchange

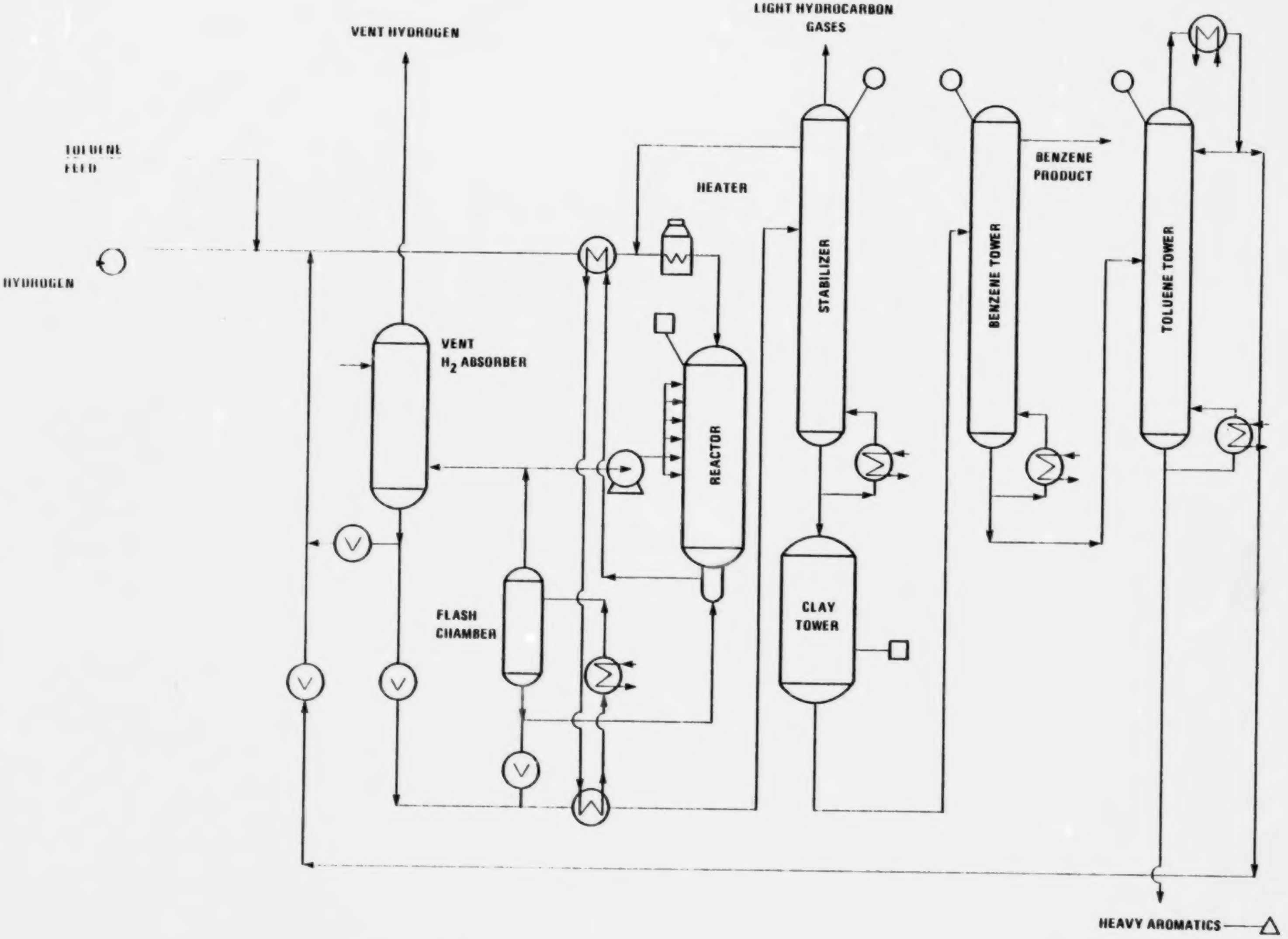


FIGURE 13.2 BENZENE PRODUCTION BY HYDRODEALKYLATION

SOURCE: EHRLICH ET AL, 1973

with fresh feed (Parsons 1977). The dealkylated product is then treated in a flash chamber which acts as a partial condenser and a gas-liquid separator. The flash chamber is a quench tower where the entering gases either condense and fall to the bottom or remain as gases and rise to the top. A hydrogen rich gas stream is passed overhead, and the liquid product leaves the bottom of the flash chamber.

The overhead vapor (contaminated with benzene and toluene gases) is passed into a hydrogen absorber for hydrogen purification. The hydrogen absorber uses a scrubbing liquid which separates the benzene for recyclying while the hydrogen is passed overhead and vented.

13.3.1.1 Emissions from Dealkylation

The dealkylation reactors are used interchangeably for reaction, regeneration, and purge. Catalyst beds need to be regenerated because of carbon (coke) deposits on the catalyst surfaces that results from organic chemical decomposition at high temperatures. According to JRB (1980), coking occurs and needs to be burned off every 2,000 to 4,000 hours. Complete burning is generally assumed, but if it does not occur, carbon monoxide is released. Therefore, emissions include carbon dioxide, carbon monoxide, hydrocarbon gases, coke fines, and catalyst fines.

When the catalyst is spent, whole catalyst beds are removed and replaced (Hydrocarbon Processes 1973). Spent catalysts are usually landfilled or processed as a by-product.

Fugitive emissions occur in the flash chamber and the vent hydrogen absorber. Some benzene escapes with the hydrogen vented to the atmosphere.

13.3.2 Stabilization

The net liquid product from the flash chamber and the vent hydrogen absorber are combined and passed into a stabilizing column. Light hydrocarbon gases, any water present in the stabilizer feed, and dissolved hydrogen sulfide (H_2S) are removed overhead (Takahashi et al. 1981, Considine 1974, and Ehrlich et al. 1973). For some processes, the light hydrocarbons are further processed for fuel; however, Ehrlich et al. (1973) reports recycling. The hydrocarbons removed have boiling points lower than that of benzene (Parson et al. 1977). The stabilizer bottoms (crude benzene fraction) contain aromatic hydrocarbons such as toluene and xylene besides the benzene. The fraction also contains heavy oil and small amounts of olefins and thiophenes (Takahashi et al 1981). The residual contaminants (olefins and thiophenes) are removed in a clay tower where activated clay is used at a temperature of 150°-230° C and at a pressure of 15-30 kg/cm^2 to maintain the benzene in a liquid phase (Takahashi et al. 1981). The olefins and thiophenes are absorbed by the clay as gases.

13.3.2.1 Emissions from Stabilization

Fugitive emissions occur at vents, valves, seals, and leaks in the equipment. The spent clay, being contaminated with sorbed olefins and thiophenes, is landfilled (JRB 1980). When brought in contact with the clay, the heavier oil in the crude benzene promotes the deterioration of the clay and shortens its life (Takahashi 1981). Thus, the clay will be replenished and landfilled frequently.

13.3.3 Distillation

The effluent from the clay tower passes to the benzene tower for distillation where the high purity benzene is removed overhead. The benzene tower also has a reboiler circuit to maintain desired separation. The bottoms containing higher aromatics are removed and passed to the toluene tower where an alkylated aromatic mixture of toluene is removed overhead. By suitable condensation and separation, a part of the toluene is returned to the tower and the net toluene removed overhead is recycled in the feed line (Ehrlich et al. 1973, Considine 1978). The bottoms are heavy aromatic products. These heavy aromatic ends are usually diphenyls and substituted biphenyls (Faith et al. 1965).

13.3.1.1 Emissions from Benzene and Toluene Distillation Columns

Fugitive emissions may result at vents, valves, seals, and leaks in the equipment. Intermittent emissions may occur at relief vents on fractionation towers. The bottoms product of heavy aromatics in sludge form is removed as a waste stream and landfilled or recycled as feed (Gusso 1981).*

13.4 SUMMARY OF EMISSION DATA

Emission points and emission types are displayed in Figure 13-2. Table 13-4 is an emissions characterization table.

No emissions data have been found on the napthalene hydrodealkylation process.

---

*Personal communication between Stan Gusso of Houdry Division, Air Products, Marcus Hook, Pennsylvania, and Patricia Wood, Versar, Inc., on August 24, 1981.

TABLE 13-4 CHARACTERIZATION OF EMISSIONS FROM THE BENZENE MANUFACTURING PROCESS

				Uncontrolled Emissions		Controlled Emissions			
Pollutant	Location (Refer to Figure 13-2)	Source	Type of Release+	Receiving Medium	Quantity kg/kg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Chromium-on-alumina	reactor	catalyst fines	r	land	NA	NA	solid	NA	NA
Platinum-on-alumina	reactor	catalyst fines	r	land	NA	NA	solid	NA	NA
Acid treated clay containing olefins and thiophens	clay tower	spent clay	r	land	NA	NA	solid	NA	NA
Aromatics, polyaromatics	process effluent	by-products	r	water	NA[3]	NA	liquid	NA	NA
Diphenyl and substituted diphenyl	toluene tower	bottom residue	r	land	NA	NA	solid	NA	NA
Benzene	-	all processes for petroleum derived benzene	r/a	air	.42[1]	NA	gas	NA	NA
				discharge to POTW	.03[1]	NA	liquid	NA	NA
				aquatic discharge	.002[1]	NA	liquid	NA	NA
	-	dealkylation process	r/a	NA	1.0[2]	NA	NA	NA	NA
Other emissions	distillation columns, flash chamber, hydrogen absorber seals, flanges, valves	-	r	NA	NA	NA	gas	NA	NA

[1] Versar, Inc. 1979. Based on 4,461,292 kkg/yr production for 1976.

[2] JRB, 1980. Based on 1,300,000 kkg/yr production for 1978.

[3] Wise and Fahrenthold, 1981. Taken from Table 3. Pollutant concentrations of at least 0.5 ppm were reported. Toluene was the feed.

NA - not available

+ Denotes that a release is routine (r) or accidental (a)

REFERENCES

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Ehrlich, S. W., and S. S. Chazanow. 1973. Hydrodealkylation. Patent No. 3,754,045.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals. 3rd Ed. New York: John Wiley and Sons, Inc.

Herrick, E. C., J. A. King, R. P. Quellette. 1979. Unit Process Guide to Organic Chemical Industries.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

JRB Associates. 1980. Level II Materials Balance - Benzene. For: Office of Pesticides and Toxic Substances, survey and Analysis Division. Washington, D. C.: U.S. Environmental Protection Agency. Draft Report.

Kirk-Othmer. 1979. Encyclopedia of Chemical Technology. 3rd Ed. Volume 3. New York: John Wiley and Sons.

Parsons, T. B., C. M. Thompson, and G. E. Wilkins. 1977. Industrial Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Radian Corporation. For: Office of Research and Development, Industrial Environmental Research Laboratory. Research Triangle Park, North Carolina: U.S. Environmental Protection Agency. EPA-600/2-77-023e.

Takahashi, H., Y. Matsuoka, and S. Hamanishi. 1981. Process for Producing High Purity Benzene. Patent No. 4,247,729.

USITC. 1979. United States Production and Sales. Synthetic Organic Chemicals. U.S. Department of Commerce.

Versar, Inc. 1979. Production and Use of Benzene. For: Office of Water Planning and Standards. Washington, D. C.: U.S. Environmental Protection Agency.

Versar, Inc. 1980. Environmental Assessment of Priority Pollutants. Task 15: Preparation of Standard Pollutant Tabs. EPA Contract No. 68-01-3852. For: Office of Water Planning and Standards. Washington, D. C.: U.S. Environmental Protection Agency.

Wise, Hugh E. Jr. and Paul D. Fahrenthold. November 1981. Priority Pollutants from Petrochemical Processes, Environmental Science and Technology, 15, (11), pp. 1242-1304.

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SECTION 14

HYDROGENATION

14.0 INTRODUCTION

Hydrogenation is the unit process in which hydrogen is added to various compounds. Almost all hydrogenation reactions involve catalysts. From a survey of hydrogenation processes, some of the common catalysts were found to be nickel, platinum, lead, cobalt, silica, zinc, iron, and ruthenium. The operating conditions were found to range from 150°C to 400°C and 0.1 MPa (9.87 x 10^{-4}) to 10 MPa (9.87 x 10^{-2}atm). The reactions take place in the liquid and vapor phases (Herrick 1979a; Shreve 1967; Kirk-Othmer 1979; Considine 1974).

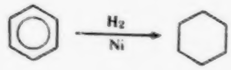
The hydrogenation processes are similar. The major operations are a catalytic reactor and a purification system. Figure 14-1 is a typical process diagram. The principal organic chemicals manufactured by hydrogenation are listed in Table 14-1.

14.1 GENERAL CHEMISTRY

Hydrogenation is used to treat many compounds. It may be used as a direct addition of hydrogen to a double or a triple bond of an unsaturated molecule.

$$CH_3C{\equiv}CH \xrightarrow[Pd]{H_2} CH_3CH{=}CH_2$$

$$CH_3CH{=}CH_2 \xrightarrow[Ni]{H_2} CH_3CH_2CH_3$$



An alkene can also react with hydrogen using a catalyst in the production of aldehydes and of alcohols.

$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\substack{20.3\ MPa\\(200\ atm)}]{150°C} RCH_2CH_2CHO$$

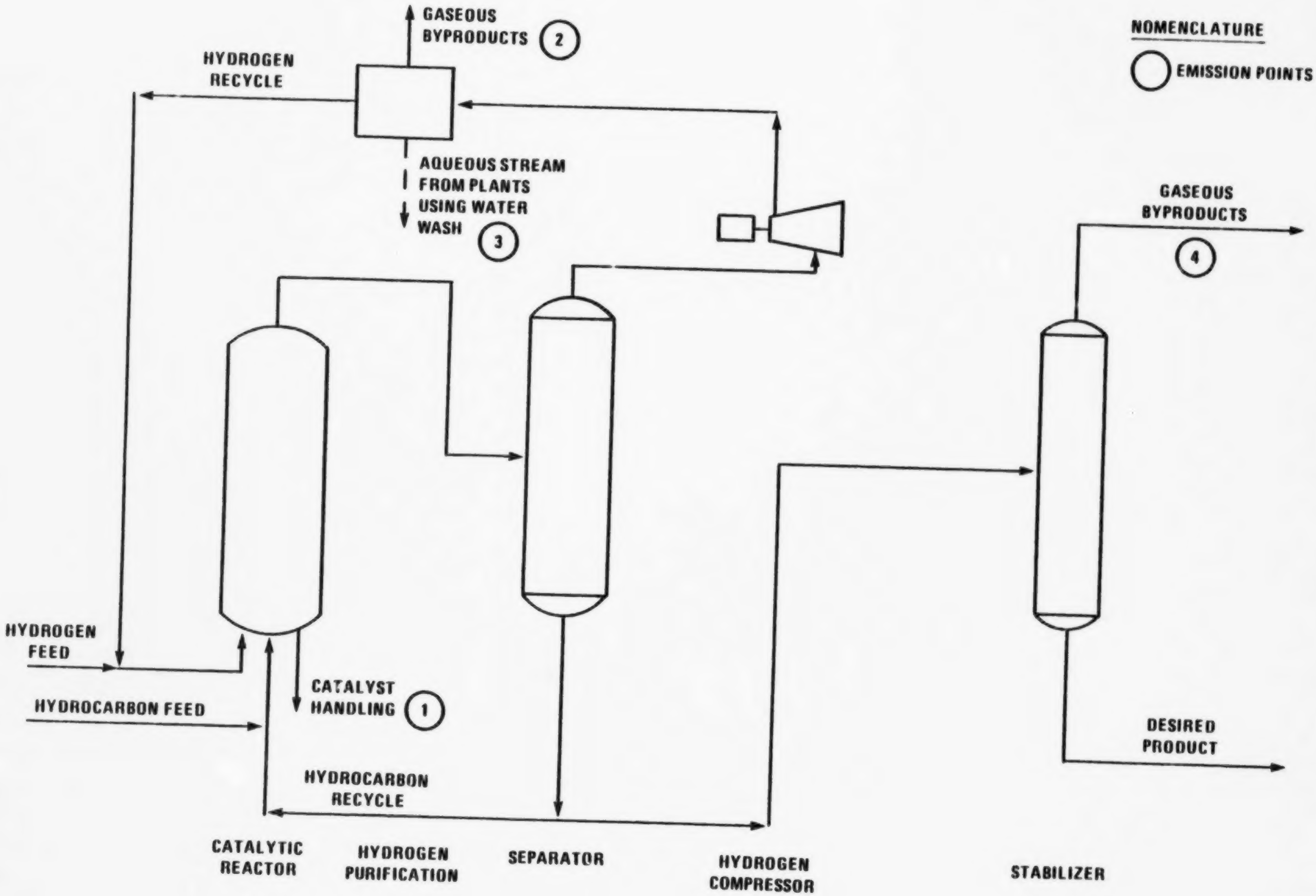


FIGURE 14-1. FLOW CHART FOR A TYPICAL HYDROGENATION PROCESS

TABLE 14-1. HYDROGENATION PRODUCTS AND THEIR PRODUCTION IN 1979

Product	Amount kkg	Feedstock	Other Required Processes
Adiponitrile	NA	butadiene	ammoxidation halogenation
m-Aminophenol	NA	nitrobenzene	hydrolysis sulfonation
p-Aminophenol	NA	nitrobenzene	acid rearrangement
Aniline	310,402	nitrobenzene	none
1,3-bis(aminomethyl) cyclohexane	NA	isophthalonitrile	none
n-Butanol n-Butyraldehyde	344,924 427,791	propylene carbon monoxide	carbonylation (oxo)
Caprolactam	425,428	toluene, ammonia	acid rearrangement oxidation
Crotonaldehyde n-Butyraldehyde n-Butyl alcohol	NA 427,791 344,924	acetaldehyde	condensation dehydration
Cyclohexane	1,091,376	benzene	none
Cyclohexanol	NA	phenol	none
Cyclohexylamine	NA	aniline	none
Cyclohexylamine	NA	nitrobenzene	
3,3'-Dichlorobenzidine dihydrochloride	NA	1-chloro-2-nitrobenzene	benzidene rearrangement
2-Ethylhexanol n-Butanol Isobutyraldehyde	NA 344,924 NA	carbon monoxide propylene	carbonylation (oxo)
2-Ethylhexanol	NA	acetaldehyde	condensation
Hexamethylenediamine	NA	adiponitrile	none

TABLE 14-1. HYDROGENATION PRODUCTS AND THEIR PRODUCTION IN 1979 (CONTINUED)

Product	Amount kkg	Feedstock	Other Required Processes
Hexamethylenediamine	NA	adipic acid ammonia	ammoxidation
Hydrazobenzene (sym-N,N'-diphenylhydrazine)	NA	nitrobenzene	condensation
Isobutyl alcohol	NA	propylene	carbonylation (oxo)
Isoprene (2-methyl-1,3-butadiene)	246,589	acetone acetylene	condensation dehydration
N-Isopropyl-N'-phenyl-p-phenylenediamine	NA	acetone aniline p-chloronitrobenzene	alkylation condensation dehydrogenation
DL-Methionine	NA	acrolein cyanic acid methyl mercaptan	condensation
2-Methyl-2-butanol	NA	acetone acetylene	condensation
Methyl isobutyl ketone	NA	acetone	condensation dehydration
Sorbitol (1,2,3,4,5,6-hexanehexol)	115,167	corn sugar or corn syrup	none
Toluene diisocyanate (TDI) (80/20-2,4-2,6-TDI)	309,170	phosgene toluene	nitration phosgenation
m-Xylenediamine	NA	isophthalonitrile	none

Sources: Herrick 1979a; USITC 1979.

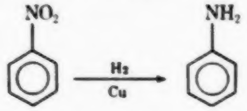
Hydrogen is added to aldehydes or to ketones to produce alcohols.

$$CH_3CH_2CH_2CHO + H_2 \xrightarrow[130\text{-}160^\circ C]{catalyst} CH_3CH_2CH_2CH_2OH$$

Hydrogenation of an acetylonic compound usually produces an alkene of cis configuration.

$$CH_3CRO + H_2 \longrightarrow CH_2 = CHR$$

A number of functional groups in organic compounds can be hydrogenated to yield different functional groups.



$$RCOOH \xrightarrow[\text{high temp and pressure}]{H_2,\ catalyst} RCH_2OH$$

$$RCHO \xrightarrow[H_2]{Pt} RCH_2OH$$

Vegatable and fish oils are hardened or solidified by catalytic hydrogenation.

$$(C_{17}H_{31}COO)_3C_3H_5 + 3H_2 \longrightarrow (C_{17}H_{33}COO)_3C_3H_5$$

The above discussion was based on information in Herrick 1975; Shreve 1967; Kirk-Othmer 1979; and Considine 1974.

14.2 DESCRIPTION OF DISCHARGES

Releases from a typical hydrogenation process occur as fugitive gaseous emissions, as vent gases, in wastewater, and as catalytic residue.

Fugitive	- pressure relief valves, pump seals, compressor seals, and drains.
Reactor	- off-gases from reactor vents.
Purification	- vents from distillation columns, bottoms from distillation columns.
Storage and Handling	- vents from feed tanks, product tanks, and loading.
Secondary	- residue from catalytic recovery.

24.3 PRODUCTION OF CYCLOHEXANE AND RESULTING EMISSIONS

Catalytic hydrogenation of benzene accounts for approximately 85% of the cyclohexane capacity in the United States. The need for low cost and high-purity hydrogen results in all production plants being located in petrochemical complexes.

The following discussion is based on information from White (1980) and is divided into the following four sections: (1) hydrogenation reactors and flash separator, (2) distillation column, (3) hydrogen purification system, and (4) emissions. There are no process emissions during normal operation, so the emissions discussion is left to the end (White 1980).

The reaction to make cyclohexane from benzene is:

$$C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$$

(benzene) (hydrogen) (cyclohexane)

Figure 14-2 shows a model-plant flow diagram.

24.3.1 Hydrogenation Reactors and Flash Separator

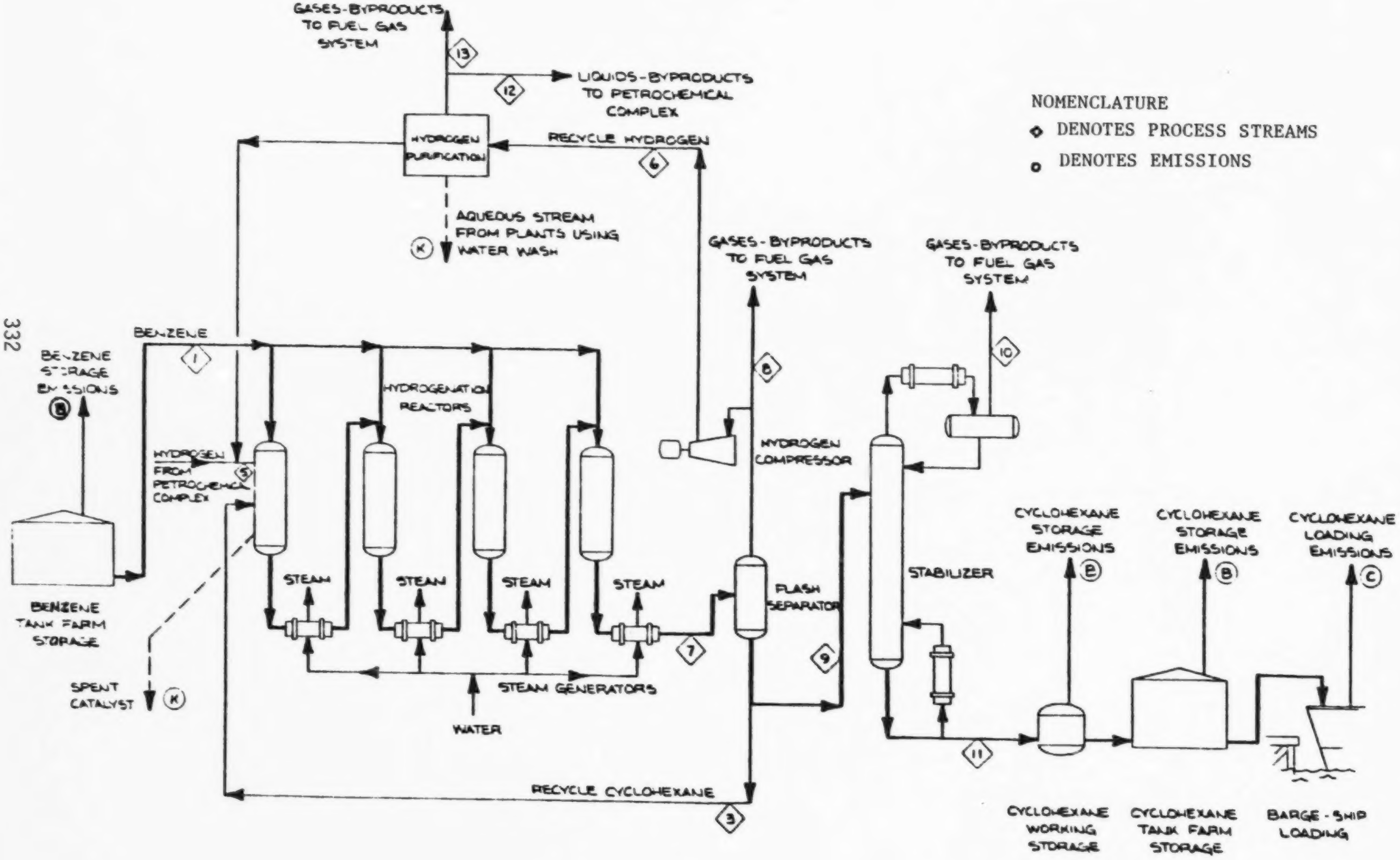
High-purity benzene is stored in large tanks and fed (Stream 1) to the catalytic reactors in parallel. Hydrogen (Stream 5) is fed into the reactors in series.

Typical temperatures and pressures in the reaction section series are 150 to 260°C and 2.1 to 3.5 MPa (2.1×10^{-2} to 3.5×10^{-2} atm). The crude cyclohexane (Stream 7) is fed into a flash separator. Since the reaction is highly exothermic, part of the cyclohexane separated in the flash separator is recycled (Stream 3) and fed to the reactors in series to control the reactor temperatures. The temperature is also controlled by generating steam for use elsewhere in the petrochemical complex.

24.3.2 Distillation Column

The cyclohexane leaving the flash separator is sent to a distillation column (stabilizer) for removal of methane, ethane, other light hydrocarbons, and soluble hydrogen gas from the cyclohexane product. These impurities (Stream 10) are routed to the complex fuel-gas storage system

FIGURE 14-2. PROCESS FLOW DIAGRAM FOR THE MANUFACTURE OF CYCLOHEXANE BY HYDROGENATION OF BENZENE



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HYDROGEN COMPRESSOR
STABILIZER
BENZENE TANK FARM STORAGE
STEAM
STEAM
STEAM
STEAM
FLASH SEPARATOR
7
9
STEAM GENERATORS
WATER
SPENT CATALYST
K
RECYCLE CYCLOHEXANE
3
11
CYCLOHEXANE STORAGE EMISSIONS
B
CYCLOHEXANE STORAGE EMISSIONS
B
CYCLOHEXANE LOADING EMISSIONS
C
CYCLOHEXANE WORKING STORAGE
CYCLOHEXANE TANK FARM STORAGE
BARGE-SHIP LOADING

NOMENCLATURE

◆ DENOTES PROCESS STREAMS

○ DENOTES EMISSIONS

and used as fuel in process heaters. Cyclohexane (Stream 11) purified in the stabilizer may be greater than 99.9% pure. The residual benzene content is typically less than 500 mg/liter. This pure product is stored in large tanks to await shipment.

24.3.3 Hydrogen Purification System

Gas from the flash separator (60 to 80 mole % hydrogen) is not pure enough for direct reuse. This gas (Stream 6) is purified to greater than 90 mole % hydrogen before being recycled (Stream 6) to the reactor. Typical processes used for hydrogen purification are adsorption and stripping of the hydrogen gas or cryogenic separation. Some plants use a combination of the two processes. Organic liquids (Stream 12) separated from the hydrogen are sent to other petroleum processing units in the complex. The separated gases (Stream 13) are used as fuel gas.

Depending on the type of hydrogen purification used, inert impurities present in the gas from the flash separator can be purged from the system before the gas enters the hydrogen purification equipment. The impurities (Stream 8) are sent to the fuel gas system. The flow and composition of stream will vary for each manufacturer depending on the hydrogen purification system.

24.3.4 Emissions

There are no process emissions during normal operation. When operations are shut down, individual equipment vents are opened as required during final depressurization of equipment. Except for the feed streams, the concentration of benzene in the process equipment is low; therefore, few or no benzene emissions would be expected during a shutdown.

Fugitive leaks can emit benzene, cyclohexane, methane, or other hydrocarbons. Leaks from heat exchangers into cooling water or steam production can be a potential fugitive loss. Fugitive losses are of special significance because of the high diffusivity of hydrogen at elevated temperature and pressure and the extreme flammable nature of the liquid and gas processing streams.

Storage emission sources (Stream B) include benzene and cyclohexane storage. In plants where adsorption is used for hydrogen purification, an additional organic compound (e.g., toluene, glycol, amine) may be stored, but the quantities of these solvents are usually small relative to the quantities of benzene and cyclohexane. Handling emissions (Stream C) relate to transfer of cyclohexane to shipping vessels.

The potential sources of secondary emissions (Stream K) are catalyst handling and absorber wastewater (where an aqueous solution is used to purify the recycled hydrogen). Caution is taken to remove the organic from the spent catalyst before it is replaced. The spent catalyst is sold for metal recovery. Plants that account for at least 16% of the total cyclohexane capacity use an aqueous solution to purify hydrogen.

24.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided in Table 14-2 for the following manufacturing processes:

- Adiponitrile
- Aniline (consult Figure 14-3 in conjunction with Table 14-2)
- n-Butanol/n-Butyraldehyde
- Cyclohexane (consult Figure 14-2 in conjunction with Table 14-2)
- Cyclohexanol (consult Figure 14-4 in conjunction with Table 14-2)
- Hexamethylenediamine

No emissions data have been found for any other hydrogenation manufacturing process.

TABLE 14-2. ESTIMATED RELEASES FOUND IN SOME HYDROGENATION PROCESSES

						Uncontrolled Emissions			Controlled Emissions		
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product	Stream Design.
Adiponitrile	hydrogen	liquid-gas separator vent	feed	r	air	1.5[1]	NA	gas	NA	NA	
	adiponitrile	thin film evaporator sludge	product	r	NA	2.65[1]	NA	solid	NA	NA	
	organic sludge	thin film evaporator sludge	by-product	r	NA	1.04[1]	NA	solid	NA	NA	
	adiponitrile	dehydrating column effluent	product	r	water	trace[1]	NA	liquid	NA	NA	
	low boilers		by-product	r	water	trace[1]	NA	liquid	NA	NA	
	high boilers	low boiler removal column effluent	by-product	r	water	trace[1]	NA	liquid	NA	NA	
	low boilers		by-product	r	water	trace[1]	NA	liquid	NA	NA	
Aniline	benzene	process vents	by-product	r	air	0.0057[2]	0.065[2]	gas	NA	NA	A
	total VOC	process vents	by-product	r	air	0.095[2]	1.08[2]	gas	NA	NA	A
	aniline and nitrobenzene	purification effluent	product and feed	r	water	NA	NA	liquid	NA	NA	D
	total VOC	storage	product feed by-product	r	air	0.023[2]	0.26[2]	gas	NA	NA	B
	total VOC	handling	product	r	air	0.0012[2]	0.014[2]	gas	NA	NA	C
n-Butanol/ n-Butyraldehyde	carbon monoxide,	catalyst recovery	feed	r	air	NA	NA	gas	NA	NA	
	propylene, and propane	section		r	air	NA	NA	liquid	NA	NA	
	heavy ends	purification section	by-products	r	air	NA	NA	gas	incinerated	NA	
	light ends	purification section	by-products	r	air	NA	NA	gas	flared	NA	
Cyclohexane	total VOC	process shutdown	NA	r	air	(0.0032)[3]	(0.02-0.09)[3]	gas	flares	NA	A
	benzene	storage	feed	r	air	(0.425-0.420)[3]	(2.42-12.0)[3]	gas	floating roofs	NA	B
	total VOC	storage	NA	r	air	(1.308-1.256)[3]	(7.47-35.9)[3]	gas	floating roofs	NA	B
	total VOC	handling	NA	r	air	(0.147-0.148)[3]	(0.84-4.22)[3]	gas	none	-	C
	benzene	fugitive	feed	r	air	(0.154-0.038)[3]	0.88[3]	gas	NA	NA	J
	total VOC	fugitive	NA	r	air	(1.419-0.284)[3]	8.1[3]	gas	NA	NA	J
	total VOC	secondary	NA	r	air	0.013[3]	(0.07-0.37)[3]	gas	API separator	NA	K

TABLE 14-2. ESTIMATED RELEASES FOUND IN SOME HYDROGENATION PROCESSES (continued)

						Uncontrolled Emissions			Controlled Emissions		
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product	Stream Design.
Cyclohexanol	benzene	hydrogenation reactor	by-product	r	air	0.0797^4	0.91^4	gas	NA	NA	A
	total VOC	hydrogenation reactor		r	air	1.52^4	17.4^4	gas	NA	NA	A
	total VOC	distillation vents		r	air	0.587^4	0.67^4	gas	NA	NA	B
	total VOC	storage and handling		r	air	0.0315^4	0.36^4	gas	NA	NA	C
	total VOC	fugitive		r	air	0.438^4	5.0^4	gas	NA	NA	D
		secondary		r	air	negligible^4	NA	gas	NA	NA	E
Hexamethylene-diamine from adiponitrile	Hexamethylenimine	stripper effluent	by-product	r	water	3.0^5	NA	liquid	NA	NA	
	1,2-cyclohexane-diamine	medium boiler stripper attachment	by-product	r	water	9.35^5	NA	liquid	NA	NA	
	heavy tar	HMDA refinery column bottoms	by-product	r	soil	41.75^5	NA	solid	NA	NA	
	acrylonitrile	process effluents	by-product	r	water	NA^6	NA	liquid	NA	NA	

Sources: [1]Hedley 1975. Based on 14,500 kkg/yr capacity.
[2]White 1980, Vol. 7. Based on 100,000 kkg/yr capacity.
[3]White 1980, Vol. 7. Based on plant capacities ranging from 50,000-250,000 kkg/yr.
[4]White 1980, Vol. 7. Based on 100,000 kkg/yr capacity.
[5]Hedley 1975. No capacity given.
[6]Wise and Farenthold 1981. Concentrations reported are greater than 0.5 ppm. Feedstock is adiponitrile.

+Denotes that a release is routine (r) or accidental (a).

FIGURE 14-3. PROCESS FLOW DIAGRAM FOR MANUFACTURE OF ANILINE

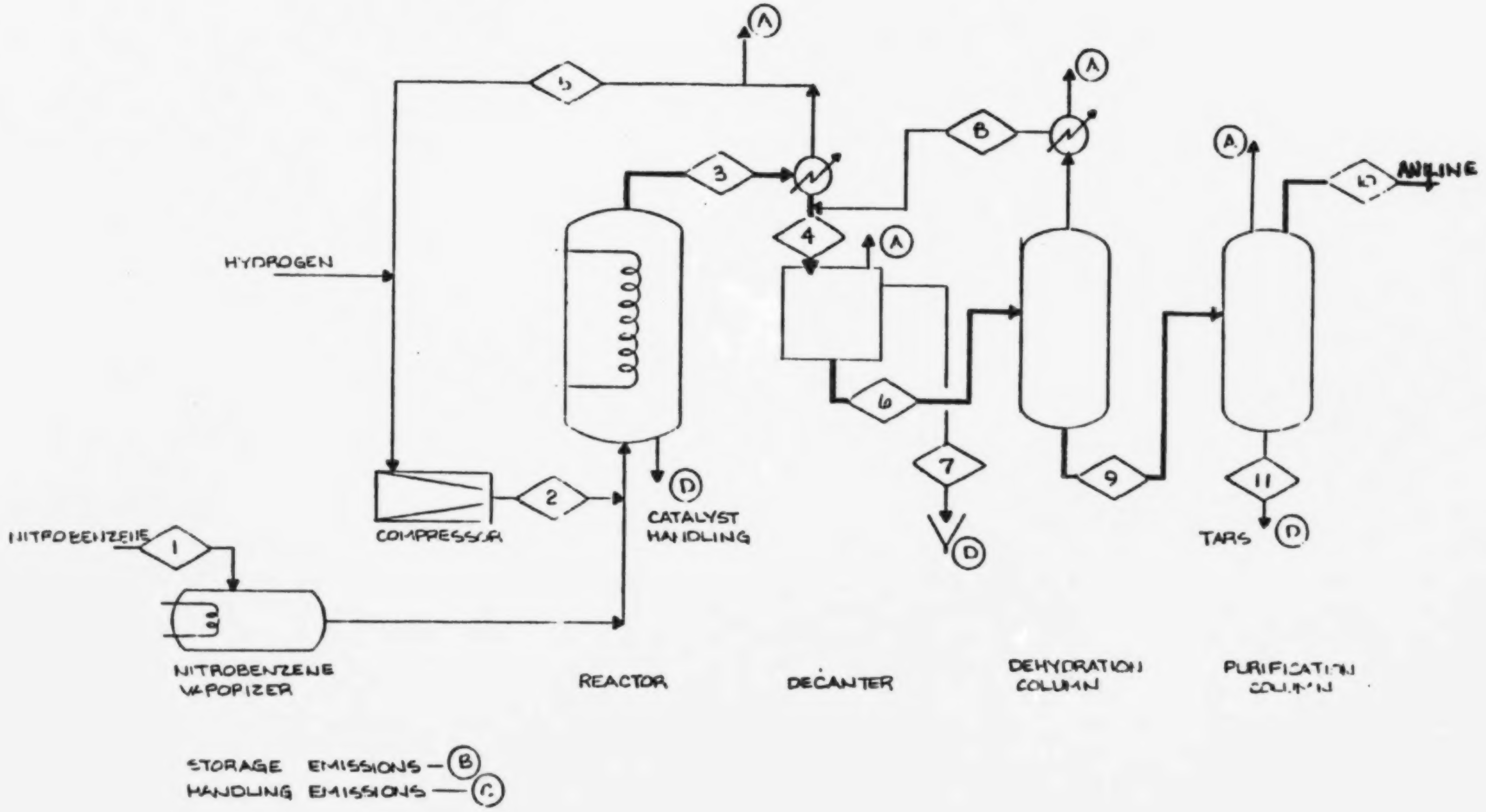
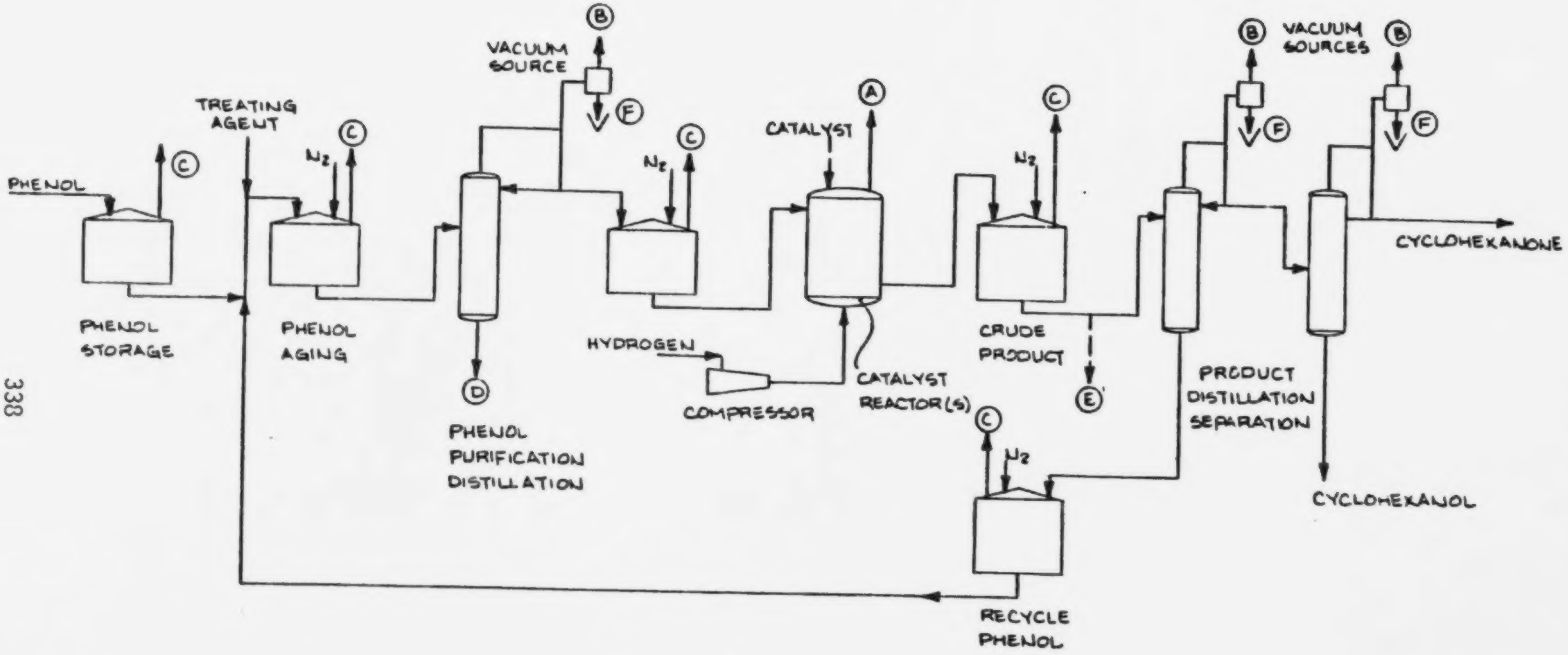


FIGURE 14-4. PROCESS FLOW DIAGRAM FOR UNCONTROLLED MODEL PLANT PRODUCING CYCLOHEXANONE/CYCLOHEXANOL BY PHENOL HYDROGENATION



REFERENCES

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals, 3rd Ed. New York: John Wiley and Sons, Inc.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. U.S.Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitg, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Company, Inc.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Kirk-Othmer. 1979. Encyclopedia of Chemical Technology, 3rd Ed., Volumes 2 and 4. New York: John Wiley and Sons, Inc.

Parsons, T. B., C. M. Thompson, and G. E. Wilkins. 1977. Industrial Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Radian Corporation. For: Office of Research and Development, Industrial Environmental Research Laboratory. Research Triangle Park, North Carolina: U.S. Environmental Protection Agency. EPA-600/2-77-023e.

Shreve, R. N. 1967. Chemical Process Industries, 3rd Ed. New York, New York: McGraw Hill Book Company.

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

U.S. EPA. 1981. Supplement 12 for Compilation of Air Pollutant Emission Factors. Research Triangle Park, North Carolina: U.S. EPA, Office of Air and Water Management and Office of Air Quality Planning and Standards.

USITC. 1979. United States Production and Sales. Synthetic Organic Chemicals. U.S. Department of Commerce.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 10. U.S.Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028e.

REFERENCES (continued)

Wise, H. and Fahrenthold, p. November 1981. Predicting Priority Pollutants from Petrochemical Processes. Environ. Sci. and Techn., Vol. 15, (11), pp. 1292-1304.

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SECTION 15

HYDROHALOGENATION

15.0 INTRODUCTION

Hydrohalogenation is the process in which a halogen atom is added to an organic compound with a halogen acid, e.g., hydrogen chloride, acting as the halogenating agent (Herrick 1979). Table 15-1 presents chemicals produced, other processes required, required feedstock, and production volumes for products that could be manufactured by the hydrohalogenation process.

The production process is catalytic for all chemicals produced by hydrohalogenation with the exception of methyl bromide and choline chloride. Typical catalysts, depending upon which chemical is being produced, are the following:

- mercuric chloride
- ferric chloride
- alumina gel
- zinc chloride on pumice
- cuprous chloride
- activated carbon

Production can be either a liquid or a vapor phase process depending upon the chemicals produced. The basic steps for this process are hydrohalogenation (mixing of the organic compound with the halogen in the presence of a catalyst in a reactor), separating the crude product, and further purification by distillation. A typical hydrohalogenation process (the manufacture of vinyl chloride monomer using hydrogen chloride and acetylene as feedstock) is shown on Figure 15-1.

Some of the major chemicals produced by hydrohalogenation such as 1,1,1-trichloroethane, methyl bromide, methyl chloride, vinyl chloride, and ethyl chloride are included in the Environmental Protection Agency's 129 priority pollutants. 1,1,1-Trichloroethane is toxic to humans and aquatic life. Its presence in drinking water and foodstuffs and its effect on the central nervous system in humans form the basis for environmental concern (EPA 1981).

TABLE 15-1. HYDROHALOGENATION PRODUCTS AND THEIR MANUFACTURE

Product	Amount kkg	Feedstock	Other Required Processes
Choline chloride	26,100[2]	ethylene oxide trimethylamine	amination by ammonolysis, condensation
Ethyl chloride	264,000[2]	ethylene	
Isoprene	248,560*[2]	formaldehyde isobutylene	condensation pyrolysis
Methyl bromide	16,640[3]	methanol	
Methyl chloride	209,900[2]	methanol	
1,1,1-Trichloroethane	324,900[2]	vinyl chloride	halogenation
Vinyl chloride monomer	108,880[1]	acetylene	

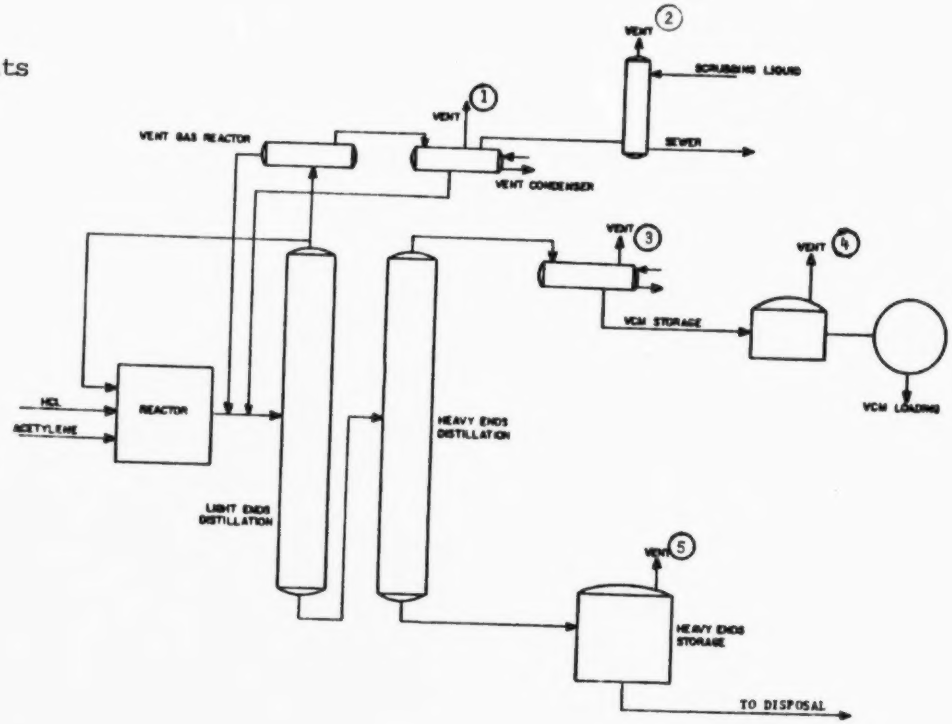
Source: Herrick et al. 1979.
[1]SRI 1981.
[2]USITC 1979.
[3]USITC 1977.

*Assumes 100% by pyrolysis.

FIGURE 15-1. A TYPICAL HYDROHALOGENATION PROCESS: MANUFACTURE OF VINYL CHLORIDE FROM ACETYLENE AND HYDROGEN CHLORIDE

Nomenclature

○ Emission Points



Source: Carpenter 1974.

Methyl bromide will produce cardiac arrest and irritation to the central nervous system in mammals.

Methyl chloride is not considered a highly toxic chemical, but reports of inhalation poisoning are numerous (EPA 1980).

Ethyl chloride is considered the least toxic of the chloroethanes; however, as a halogen containing hydrocarbon, it is potentially damaging to the liver and is known to disturb cardiac rhythm (EPA 1980).

There are numerous clinical indications that chronic exposure to vinyl chloride is toxic to humans. It is a human and animal carcinogen (EPA 1980).

15.1 GENERAL CHEMISTRY

The production of methyl chloride from methanol and hydrogen chloride is a typical example of a chemical produced by hydrohalogenation. Methylchloride is produced by the action of hydrogen chloride on methanol in the presence of a catalyst at atmospheric pressure, in the liquid or the vapor phase. The chemistry of this exothermic reaction is:

$$CH_3OH + HCl \xrightarrow[180\text{-}350^\circ C]{\text{catalyst}} CH_3Cl + H_2O$$

Most 1,1,1-trichloroethane is produced domestically using vinyl chloride as the principal feedstock (White 1980). In a two-step process, vinyl chloride is hydrochlorinated with the aid of a catalyst to produce the dichloroethane intermediate. The dichloroethane is thermally chlorinated to produce 1,1,1-trichloroethane. The chemical reactions are illustrated below.

(1) $CH_2 = CHCl + HCl \xrightarrow[35\text{-}40^\circ C]{FeCl_3} C_2H_4Cl_2$

(2) $C_2H_4Cl_2 + Cl_2 \xrightarrow[400^\circ C]{} CH_3CCl_3 + HCl.$

15.2 DESCRIPTION OF DISCHARGES

Releases from a typical hydrohalogenation process will result as fugitive emissions from process pumps, compressor seals, process valves, pressure relief valves, cooling towers, and drains. When process pressures are higher than cooling water pressures, VOC can leak into the cooling and escape as a fugitive emission from the cooling towers (White 1980). Pollutants are also released from purging catalysts beds and catalysts regeneration. Waste is also generated from the removal of spent catalysts. The disposal of catalyst residue in landfills and the combustion of organic wastes are sources of emissions.

Product separation and purification result in fugitive and intermittent emissions, and heavy polymeric matter (Faith et al. 1965). Emissions can occur when wastewater from process sources is sent to wastewater treatment systems and the VOC is desorbed.

15.3 PROCESS DESCRIPTION: PRODUCTION OF ETHYL CHLORIDE

Most of the ethyl chloride produced domestically is manufactured by using ethylene and hydrogen chloride as feedstock. The best available information for the production process is found in Gruber 1975 and Faith et al. 1965. Figure 15-2 is a flow diagram for ethyl chloride production from ethylene, and Table 15-2 presents some of its properties.

Ethyl chloride is produced by the reaction of anhydrous hydrogen chloride with ethylene in the presence of a catalyst. This continuous hydrochlorination process can take place either in a vapor or liquid phase to give up to 95% yield ethyl chloride.

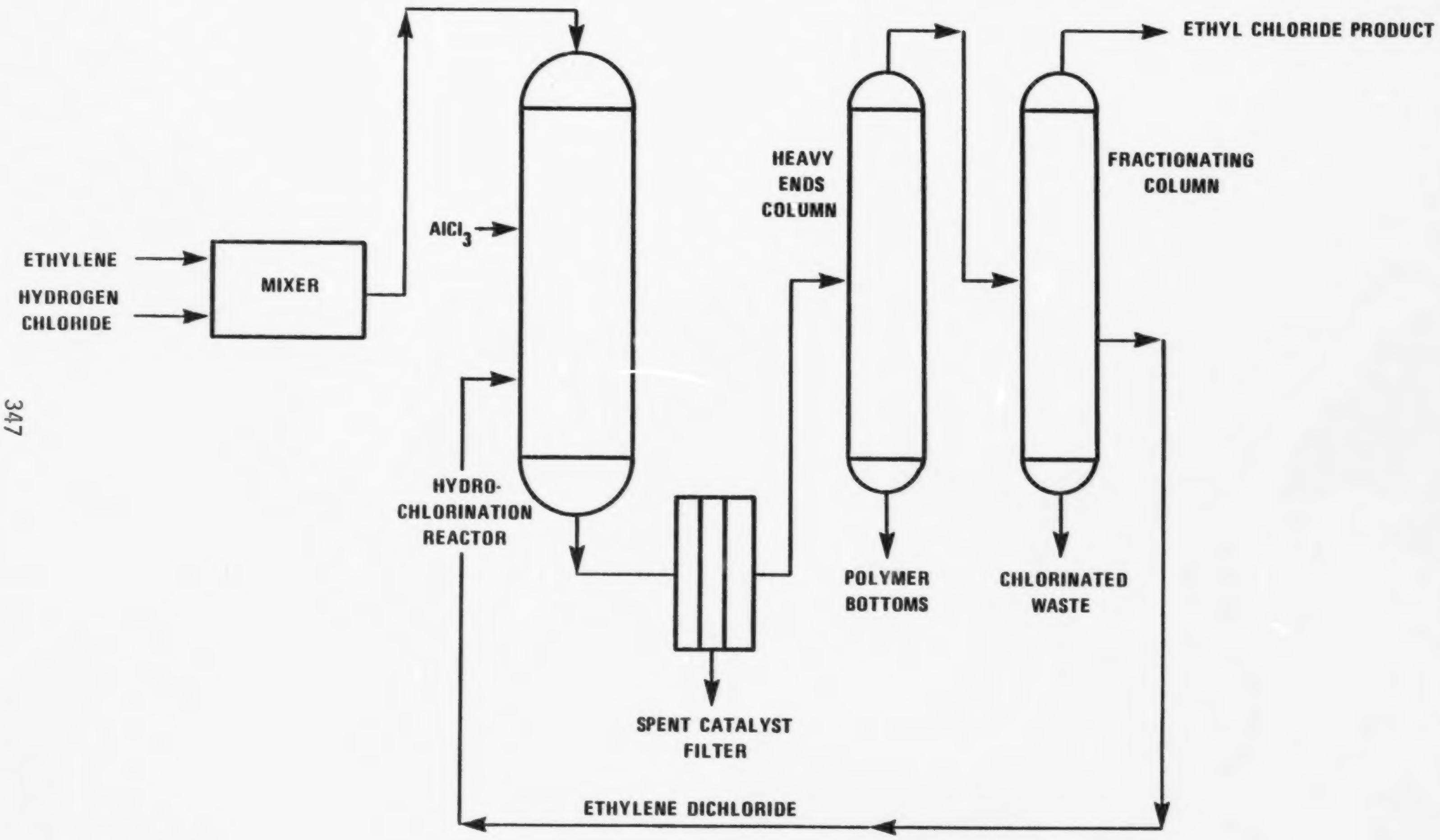
The chemical reaction is as follows:

$$C_2H_4 + HCl \xrightarrow[35\text{-}40^\circ C]{AlCl_3} C_2H_5Cl$$

The three basic steps for the production of ethyl chloride from a ethylene are:

- hydrochlorination
- product separation
- product purification

FIGURE 15-2 MANUFACTURE OF ETHYL CHLORIDE FROM ETHYLENE AND HYDROGEN CHLORIDE



SOURCES: WHITE, 1980; GRUBER 1975; FAITH ET AL. 1965.

TABLE 15-2. SOME PROPERTIES OF ETHYL CHLORIDE

Molecular weight	64.52
Boiling point	12.27°C
Melting point	-138.3°C
Specific gravity	0.917
Vapor pressure	1,000 mm @ 20°C
Flash point (closed up)	-58°F

Soluble in alcohol, ether, and most hydrocarbon solvents.

Source: Faith et al. 1965.

15.3.1 Hydrochlorination

Ethylene gas and anhydrous hydrogen chloride are mixed in equimolecular portions and passed into a hydrochlorinator reactor. The reaction is exothermic and takes place at approximately 35 to 40°C in the presence of a catalytic amount of aluminum chloride. The yield of polychloro compounds is reduced by the addition of ethylene dichloride to the reaction mixture.

15.3.1.1 Emissions from Hydrochlorination

The reaction produces spent catalyst from the reactor. Emissions will occur from the continual withdrawal of the spent catalyst to add the new makeup catalyst. The residue is usually disposed of in landfill. However, for some processes, the spent catalyst is regenerated and recycled.

15.3.2 Product Separation

The vaporized hydrocarbon products from the reactor are fed into a heavy ends column where the low boiling ethyl chloride is separated from the heavier polymers. The reaction produces a hydropolymer oil by-product that is removed from the bottom of the heavy ends column.

15.3.2.1 Emissions from Separation

Gaseous process emissions are vented from the distillation columns reflux condensers. The by-product hydropolymer oil is sold.

15.3.3 Product Purification

The overhead stream of crude ethyl chloride from the heavy ends column passes to the fractionating column, where a separation is made between the chlorinated hydrocarbon tails and the ethyl chloride.

The hydrocarbon tails are removed from the bottom and usually consist of 3 percent ethyl chloride, 22 percent dichloroethane, 32 percent trichloroethylene, and 43 percent heavy chlorinated organics (Gruber 1975). The purified product stream is passed overhead.

15.3.3.1 Emissions from Product Purification

Emissions will occur from distillation column vents. The fractionating column tails are sent to chlorinated solvent manufacture. The heavy chlorinated organics part of the hydrocarbon tails, present emissions only after discharge to landfills as a distillation residue from the solvent process line. These distillation residues are mixed heavy chlorinated hydrocarbons of hexachlorobutadienes, chlorobenzenes, chloroethanes, chlorobutadienes, and tars. These wastes constitute a hazardous waste stream because of the toxicity of chlorobenzene, chloroethane, and hexachlorobutadiene.

15.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the following manufacturing processes:

- Ethyl chloride (Table 15-3, Figure 15-2)
- 1,1,1-Trichloroethane (Table 15-4, Figure 15-3)
- Vinyl chloride (Table 15-5, Figure 15-1)
- Choline Chloride (Table 15-6)

Releases are characterized as either routine (r) or accidental (a), controlled or uncontrolled. Emissions data have not been found for any other hydrohalogenation manufacturing processes.

TABLE 15-3. CHARACTERIZATION OF EMISSIONS FROM THE ETHYL CHLORIDE MANUFACTURING PROCESS

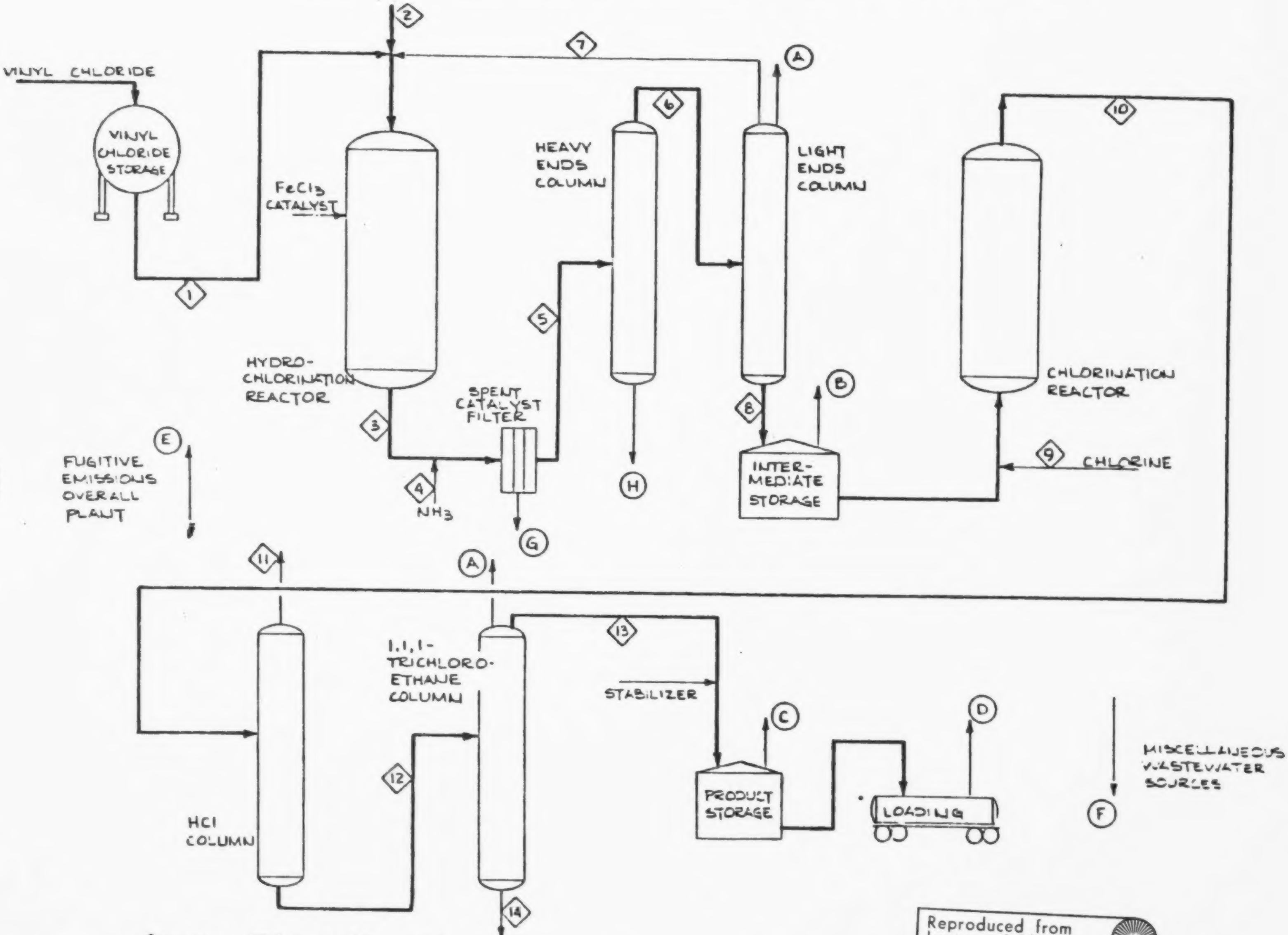
					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Consult Figure 15-2)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Ethyl chloride	fractionating column waste	product	r	air	3	NA	liquid	NA	NA
Trichloroethylene	fractionating column waste	by-product	r	land	30	NA	liquid	NA	NA
Dichloroethane	fractionating column waste	by-product	r	land	20	NA	liquid	NA	NA
Hexachlorobutadiene	fractionating column waste	by-product	r	land*	30.8	NA	liquid	NA	NA
Chlorobenzene	fractionating column waste	by-product	r	land*	2.8	NA	liquid	NA	NA
Chloroethane	fractionating column waste	by-product	r	land*	1.2	NA	liquid	NA	NA
Chlorobutadiene	fractionating column waste	by-product	r	land*	1.2	NA	liquid	NA	NA
Tars and residue	fractionating column waste	by-product	r	land*	2.8	NA	residue	NA	NA
Hydropolymer bottoms	separator	by-product	r	-*	20	NA	oil	NA	NA

Source: Gruber, TRW 1975. Based on a typical train of 90,000 kkg production capacity per year.

+Denotes that a release is routine (r) or accidental (a).

*The fractionating column tails are sent to solvent manufacturing. The heavy chlorinated organics portion is disposed to land as a result of disposal from solvent production. The polymer oil is sold.

FIGURE 15-3. MANUFACTURE OF 1,1,1-TRICHLOROETHANE FROM VINYL CHLORIDE



Source: White, 1980. Vol. 8.

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TABLE 15-4. ESTIMATES OF EMISSIONS FROM THE 1,1,1-TRICHLOROETHANE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (Consult Fig. 15-3)	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Vinyl chloride	steam stripper	feedstock	r	air	$.50^2$	NA	gas	NA	NA
	distillation vent A	feedstock	r	air	$.0019^1$	3.0^1	gas	combustion in incinerator	$.004^3$
Ethylene dichloride	distillation vent A	by-product	r	air	$.0048^1$	3.0^1	gas		
Oxygen, nitrogen	distillation vent A	by-product	r	air	$.1848^1$	3.0^1	gas		
Carbon dioxide	distillation vent A	by-product	r	air	$.0019^1$	3.0^1	gas		
VOC	steam stripper	NA	r	air	$.001^1$	$.02^1$	gas	none	$.001^1$
VOC	incineration of liquid residue	NA	r	air	$<.001^1$	$<.01^2$	gas	none	$<.001^1$
Dichloroethane	steam stripper	by-product	r	air	$.5^2$	NA	gas	NA	NA
	hydrochlorinator	by-product	r	air	8.5^2	NA	gas	NA	NA
1,1,1-Trichloroethane	steam stripper	product	r	air	$.5^2$	NA	gas	NA	NA
	hydrochlorinator	product	r	air	9.0^2	NA	gas	NA	NA
HCl and organic chlorides	steam stripper	feed	r	water	traces^2	NA	liquid	NA	NA

Sources: [1] White 1980, Volume 8. Based on 136,000, kkg production per year.
[2] Hedley et al. 1975. Production basis not stated.
[3] Total for all pollutants from all the distillation vents (A) in the process (White 1980, Vol. 8).

+Emissions are routine (r) or accidental (a).

TABLE 15-5. CHARACTERIZATION OF EMISSIONS FROM THE VINYL CHLORIDE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Acetylene	stabilizer	feedstock	r	air	1.6^1	NA	gas	NA	NA
Hydrogen chloride	stabilizer	by-product	r	air	2.8^1	NA	gas	NA	NA
Vinyl chloride	stabilizer	product	r	air	5.3^1	NA	gas	NA	NA
	reactor vent	product	r	air	3.5^2	53.3^2	gas	NA	NA
	heavy ends storage	product	r	air	$.75^2$	NA	gas	NA	NA
	fugitive emissions from pumps, valves, etc.	product	a	air	1.5^2	22.7^2	gas	NA	NA

Source: [1]Hedley 1975. Based on 45,359 kkg per year capacity.
[2]Carpenter 1974.

+Emissions are routine (r) or accidental (a).

TABLE 15-6. ESTIMATES OF EMISSIONS FROM THE CHOLINE CHLORIDE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Trimethylamine	NA	feedstock	r	NA	1.5	NA	NA	NA	NA

Source: EPA 1981, Organic Chemical Producers Data Base.

+ Emissions are routine (r)

REFERENCES

Carpenter, B. H. 1974. Vinyl Chloride - An Assessment of Emissions Control Techniques and Costs. U.S. EPA. Prepared for RTP, North Carolina: EPA-650/2-74-097.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals. 3rd Ed. New York, New York: John E. Wiley and Sons, Inc.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides, and Explosives Industries. U.S.Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Technomic Publishing Company, Inc. Westport, Connecticut.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science.

U.S. EPA. 1975. Production, Distribution, Use, and Environmental Impact Potential of Selected Pesticides. Washington, D. C.: Office of Pesticide Programs. Office of Water and Hazardous Materials.

U.S. EPA. 1980a. Ambient Water Quality Criteria for Chlorinated Ethanes. Washington, D. C.: Office of Water Regulations and Standards, Criteria and Standards Division.

U.S. EPA. 1980b. Ambient Water Quality Criteria for Vinyl Chloride. Washington, D. C.: Office of Water Regulations and Standards, Criteria and Standards Division.

U.S. EPA. 1980c. Ambient Water Quality Criteria for Halomethates. Washington, D. C.: Office of Water Regulations and Standards, Criteria and Standards Division.

U.S. EPA. Office of Solid Waste, November 14, 1980. Background Document. Resource Conservation and Recovery Act, Subtitle C - Identification and Listing of Hazardous Waste, pp. 261.31 and 261.32. Listing of Hazardous Wastes (Finalization of May 19, 1980 Hazardous Waste List, pp. 320-335).

U.S. EPA. 1981. Standard Pollutant Tab for 1,1,1-Trichloroethane. Washington, D. C.: Office of Water Regulations and Standards, Monitoring and Data Support Division.

REFERENCES (continued)

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

USITC. 1977. United States Production and Sales. Synthetic Organic Chemicals. U.S. Department of Commerce.

USITC. 1979. United States Production and Sales. Synthetic Organic Chemicals. U.S. Department of Commerce.

U.S. EPA. 1981. Organic Chemical Producers Data Base.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 8. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028c.

REFERENCES EVALUATED BUT NOT CITED

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Kirk-Othmer. 1979. Encyclopedia of Chemical Technology. 3rd Ed., Volume 13. New York: John Wiley and Sons.

Tracor Jitco. 1976. Production and Use of Chloroethanes: Chapter 5. Draft Report. Washington, D. C.: U.S. Environmental Protection Agency.

Traco Jitco. 1976. Production and Use of Halomethanes. Chapter 5. Draft Report. Washington, D. C.: U.S. Environmental Protection Agency.

Versar, Inc. 1979. Production and Use of 1,1,1-Trichloroethane. For: Office of Water Planning and Standards. Washington, D. C.: U.S. Environmental Protection Agency.

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SECTION 16

HYDROLYSIS AND HYDRATION

16.0 INTRODUCTION

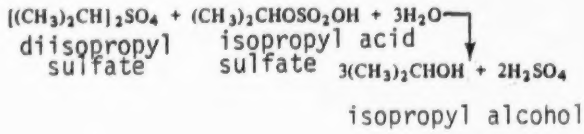
Hydrolysis is the process by which an organic feedstock is reacted with water to form one or more new chemical compounds. The reaction occurs at moderately high temperatures and pressures, 150 to 500°C and 60 to 100 atm, respectively. The reactor is usually a catalytic bed, containing ion-exchange catalysts such as phosphoric acid in diatomaceous earth or catalytically active silicic acid (Faith et al. 1965).

A typical hydrolysis process is shown in Figure 16-1. After the reaction takes place, the effluent is sent to a separator where the gas phase and the liquid phase (product in solution with water) are separated and sent to their respective treatment systems. The gas phase, mostly product, enters a scrubber where it is scrubbed with water and discharged as bottoms, in solution with water. The bottoms from the separator and scrubber are distilled to remove light and heavy impurities. Following purification, the product is sent to a dehydrator to remove the water (Hydrocarbon Processing 1973).

Hydrolysis products and their 1980 production levels are found in Table 16-1.

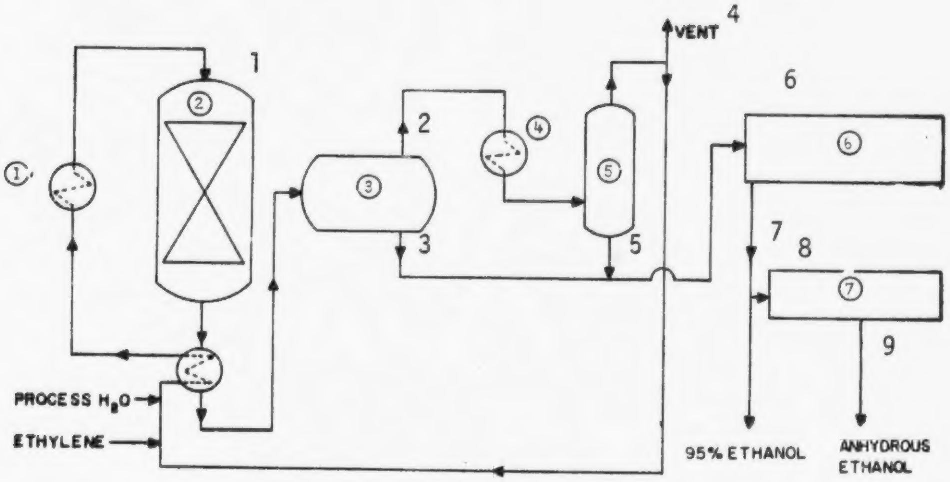
16.1 GENERAL CHEMISTRY

Water reacts with another substance to form two or more new substances. Water is ionized and the compound that is hydrolyzed is split, with H^+ going to one of the new substances and OH^- to the other (Herrick et al. 1979).



$$[(CH_3)_2CH]_2SO_4 + (CH_3)_2CHOSO_2OH + 3H_2O \rightarrow 3(CH_3)_2CHOH + 2H_2SO_4$$

FIGURE 16-1. GENERAL HYDROLYSIS PROCESS



1) heater
2) reactor
3) separator
4) cooler
5) scrubber
6) D.C.
7) dehydrator

TABLE 16-1. HYDROLYSIS PRODUCTS AND THEIR PRODUCTION IN 1980

Product	Amount* kkg	Feedstock	Other Required Processes
Acetic acid, methanol	711,233	Methyl acetate	
Acrylamide	54,431	Acrylonitrile	
Alcohols, mixed linear sulfate ammonium salt sodium salt triethanolamine salt unspecified salts	NA	Fatty alcohols, sulfur trioxide	sulfonation
Alkylbenzene sulfonate	NA	Alkylbenzenes, sulfur trioxide	sulfonation
m-Aminophenol	NA	Nitrobenzene	hydrogenation sulfonation
sec-Butyl alcohol	299,371 (feedstock not specified)	Butylene	sulfonation
sec-Butyl alcohol		Butene-1/butene-2	
Epichlorohydrin	170,551	Allyl chloride, hypochlorous acid	chlorohydrination
Ethyl alcohol	NA	Ethylene	
Ethyl alcohol, ethyl ether	23,224	Ethylene	
Ethylene glycol	1,952,262	Ethylene oxide	
Ethylene oxide, ethylene glycol	2,414,926	Ethylene	oxidation
Formic acid, sodium formate	27,215	Carbon monoxide, sodium hydroxide	carbonylation
Formic acid	27,215	Carbon monoxide (methanol recycled)	carbonylation condensation
Glycerin	14,515	Allyl alcohol, peracetic acid	epoxidation
Acetic acid	14,515	Peracetic acid	
Glycerine (glycerol)	36,287	Propylene → Allyl chloride → Epichlorohydrin	chlorohydrination halogenation

TABLE 16-1. HYDROLYSIS PRODUCTS AND THEIR PRODUCTION IN 1980 (continued)

Product	Amount* kkg	Feedstock	Other Required Processes
Isopropyl alcohol	1,025,119	propylene	sulfonation
Isopropyl alcohol		propylene	
Maleic acid(cis-1,2-ethylenedicarboxylic acid)	NA	maleic anhydride	
Methyl ethylketone	252,197	butene-1/butene-2	dedhydrogenation
Methyl methacrylate monomer	413,676	acetone, hydrogen cyanide, methanol	esterification hydrocyanation sulfonation
2-naphthol	NA	naphthalene	sulfonation
Pentachlorophenol	NA	hexachlorobenzene	
Phenol	NA	monochlorobenzene	
Phenol	NA	benzene, sulfuric acid	sulfonation
Phenol	NA	benzene, hydrogen chloride	oxyhalogenation
Phenol, acetone	1,416,297 1,909,805	benzene, propylene	acid cleavage alkylation oxidation
Propylene glycol (1,2-dihydroxypropane)	315,700	propylene oxide	
Propylene oxide	533,425 NA	propylene tert-butyl alcohol (recycled chlorine)	chlorohydrination halogenation
Propylene oxide	533,425	propylene, chlorine solution	chlorohydrination
2,4,5-trichlorophenol	NA	benzene, methanol, sodium hydroxide	halogenation

Source: SRI 1981; Herrick et al. 1979.

*SRI lists amounts in plant capacities. For this table, the capacities were multiplied by 0.8.

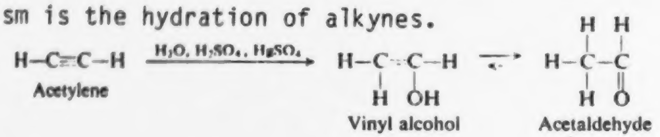
Note: The production data shown do not necessarily imply that hydrolysis in combination with the other required processes is the only product manufacturing train in commercial use.

Hydration also involves the reaction of water with another substance, but the other compound is not decomposed. The new compound contains both the hydrogen and the hydroxyl groups (Herrick et al. 1979).

$$CH_3CH{=}CH_2 + H_2O \xrightarrow[170\text{-}190^\circ C]{\text{catalyst}} (CH_3)_2CHOH$$

propylene isopropyl alcohol

Tautomerism is the hydration of alkynes.



$$H-C\equiv C-H \xrightarrow{H_2O,\ H_2SO_4,\ HgSO_4} H-\underset{H}{C}=\underset{OH}{C}-H \rightleftharpoons H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{O}{\overset{|}{C}}}$$

(enol) (keto)

There is an equilibrium between the enol and keto structures, but generally the keto form is favored (Morrison and Boyd 1973).

16.2 DESCRIPTION OF DISCHARGES

Releases from a hydrolysis process will occur as fugitive and particulate gaseous emissions and liquid wastes. The major sources of contamination are (1) gaseous emissions from vents on the reactor, scrubber, and distillation columns which pull off excess feedstock and by-products, (2) cooling water contamination from mixing in the condensers with the distillation column overhead, and (3) liquid emissions in wastestreams from the final product purification system containing excess feedstock and by-products.

Fugitive gaseous emissions - may occur from valves and process pumps; are released from contaminated cooling water supply.

Reactor - gaseous excess feedstock will be released through a vent on the reactor.

Separator - excess feedstock and by-products are released through vents in the gaseous form.

Scrubber - excess feedstock and by-products are released through vents in the gaseous form, and in the liquid form they are washed out in a wastestream.

Dehydration - excess feedstock and by-products are released through a vent in the gaseous form.

Light ends column - light impurities are released in the gaseous form through a vent.

Final product column - excess feedstock and by-products are released through a vent in the gaseous form, and in the liquid form they are washed out in a wastestream.

16.3 DESCRIPTION OF AN EXAMPLE PRODUCTION PROCESS: MANUFACTURE OF ETHYLENE GLYCOL FROM ETHYLENE OXIDE HYDROLYSIS

This description of the manufacture of ethylene glycol by the hydrolysis of ethylene oxide consists of four major steps: (1) hydrolysis reaction, (2) lights removal, (3) water removal, and (4) glycol separation and purification. Figure 16-2 illustrates this process. For each part, the description highlights the emissions associated with the step of the process.

16.3.1 The Hydrolyzer

Liquid ethylene oxide and water are mixed under pressure, preheated, and fed to the hydrolyzer. This is a noncatalyzed continuous process in the liquid phase. It is an exothermic reaction, and the reactor effluent exits at 200°C (White 1980).

16.3.1.1 Emissions

Fugitive emissions may occur at process pumps and valves (White 1980).

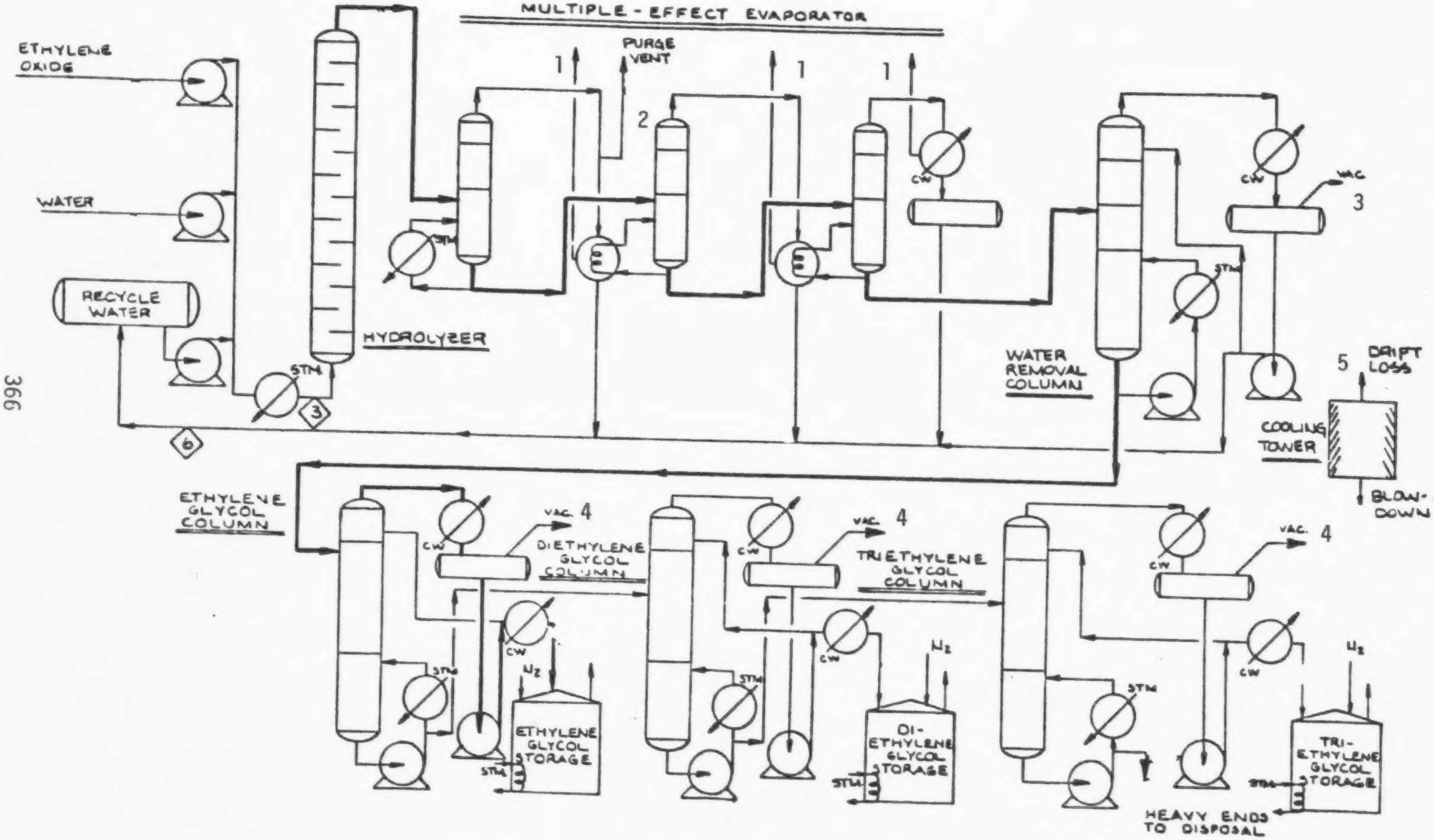
16.3.2 Lights Removal

The reactor effluent containing product, water, and impurities enters a series of distillation columns to remove light impurities from the system. The remaining vapor from the final lights removal column is condensed and recycled. Noncondensable gases are removed from the system through a vent on the final lights column (White 1980).

16.3.2.1 Emissions

Emissions occur at a purge vent on the first lights removal column. The water in the condenser may be contaminated by vent emissions. Partial desorption occurs as the cooling water passes through the cooling

FIGURE 16-2. FLOW DIAGRAM FOR UNCONTROLLED MODEL PLANT PRODUCING ETHYLENE GLYCOL BY NONCATALYZED HYDRATION OF ETHYLENE OXIDE.



water circuit and cooling towers. Fugitive emissions may occur at process pumps and valves (White 1980).

16.3.3 Water Removal

The concentrated glycol solution enters a water removal column for final drying. Water in the solution is vacuum distilled and removed overhead, where it is condensed and recycled. Glycol exits the bottom of the water removal column (White 1980).

16.3.3.1 Emissions

The steam-jet ejector through which the overhead passes discharges pollutants. The condensed water contains ethylene glycol and ethylene oxide, as well as other organic carbons. Process pumps and valves are sources of fugitive emissions. The water in the condenser may be contaminated by vent emissions (White 1980).

16.3.4 Glycol Separation and Purification

The glycol mixture enters a series of vacuum distillation columns where ethylene glycol, diethylene glycol, and triethylene glycol are removed overhead from their respective removal columns. Heavy ends from the final column bottoms are sent to disposal or sold as by-products (White 1980).

16.3.4.1 Emissions

There is a discharge at vents on the distillation columns. These emissions circulate with the cooling water and may contaminate the cooling system. Fugitive emissions may occur at pumps and valves (White 1980).

16.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the following manufacturing processes:

- Glycerin from epichlorohydrin (Table 16-2)
- Glycerin from allyl alcohol (Table 16-3)
- Ethylene glycol (Table 16-4)

TABLE 16-2. CHARACTERIZATION OF EMISSIONS FROM THE GLYCERIN MANUFACTURING PROCESS (USING EPICHLOROHYDRIN AS FEEDSTOCK)

Pollutant	Location (refer to Figure 16-1)	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg
Glycerin	effects evaporator	product	r	water	4.5^1	NA	liquid	NA	NA
Sodium chloride	certrifuge (not shown)	by-product	r	land	431^1	NA	solid	NA	NA
Glycerin	concentrator (not shown)	product	r	water	22^1	NA	liquid	NA	NA
Glycerin	film evaporator (not shown)	product	r	water	9.5^1	NA	liquid	NA	NA
Sodium chloride		by-product	r	water	82.5^1	NA	liquid	NA	NA
Light impurities		by-product	r	water	61.0^1	NA	liquid	NA	NA
Toluene	toluene recovery column-4	feedstock	r	water	4.5^1	NA	liquid	NA	NA
Glycerin	light ends	product	r	water	$.8^1$	NA	liquid	NA	NA
Toluene	column-6	feedstock	r	water	1.5^1	NA	liquid	NA	NA
Total VOC	CO_2 absorber vent (not shown)	product, by-product and feedstock	r	air	0.4^2	NA	gas	none	0.4^2
	evaporator vent (not shown)		r	air	$<0.1^2$	NA	gas	none	$<0.1^2$
	concentrator vent (not shown)		r	air	$<0.1^2$	NA	gas	none	$<0.1^2$
	stripping column-4		r	air	$<0.1^2$	NA	gas	none	$<0.1^2$
	light-ends column-6		r	air	$<0.1^2$	NA	gas	none	$<0.1^2$
	solvent column (not shown)		r	air	0.2^2	NA	gas	none	0.2^2
	product column-8		r	air	$<0.1^2$	NA	gas	none	$<0.1^2$
	cooling tower (not shown)		r	air	2.8^2	NA	gas	steam strip wastewater	0.14^2

Source: (1)Hedley et al. 1975. Based on 11431 kkg/yr capacity.
(2)White 1980, Volume 10, Section 3.

+Emissions are routine (r).

TABLE 16-3. CHARACTERIZATION OF EMISSIONS FROM THE GLYCERIN MANUFACTURING PROCESS (USING ALLYL ALCOHOL AS FEEDSTOCK)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
	(refer to Figure 16-1)								
Allyl alcohol	hydrolysis	feedstock	r	air	6[1]	NA	gas	NA	NA
butanol	section-1	by-product	r	air	2[1]	NA	gas	NA	NA
acrolein		by-product	r	air	20[1]	NA	gas	NA	NA
light impurities		by-product	r	air	22[1]	NA	gas	NA	NA
Allyl alcohol	purification	feedstock,	r	water	4[1]	NA	liquid	NA	NA
glycerin light	section-7	product &	r	water	3.5[1]	NA	liquid	NA	NA
impurities		by-product	r	water	23.5[1]	NA	liquid	NA	NA
Total VOC	light ends column-6	feedstock,	r	air	15[2]	NA	gas	scrubber	0.45[2]
	concentrator (not shown)	product,	r	air	0.15[2]	NA	gas	none	0.15[2]
	glycerin flasher	and	r	air	0.15[2]	NA	gas	none	0.15[2]
	column (not shown)	by-product							
	product column-8		r	air	0.15[2]	NA	gas	none	0.15[2]

Source: (1)Hedley et al. 1975. Based on 11657 kkg/year capacity.
(2)White 1980, Volume 10, Section 3.

+Emissions are routine (r).

TABLE 16-4. CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE GLYCOL MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
	(refer to Figure 16-2)								
BOD	dehydrator-9	by-product	r	water	.34[1]	NA	liquid	NA	NA
TOC		by-product	r	water	4.53[1]	NA	liquid	NA	NA
COD		by-product	r	water	8.77[1]	NA	liquid	NA	NA
Total VOC	lights removal 1 & 2	feedstock,	r	air	0.0595[2]	1.16[2]	gas	surface condensers	0.0062[2]
	dehydrator-3	product, &	r	air					
	purification columns-4	by-product	r	air					
	cooling tower, pumps, and valves		a	air	4.7407[2]	92.05[2]	gas	Inspection & maintenance	0.0240[2]

Source: (1)Hedley et al. 1975.
(2)White 1980, Volume 9, Report 8. Based on 170,000 kkg/yr capacity.

+Indicates that release is routine (r) or accidental (a).

- Methyl ethyl ketone (Table 16-5)
- Isopropyl alcohol (Table 16-6)
- sec-Butyl alcohol (Table 16-7)
- Ethyl alcohol (Table 16-8)
- Propylene oxide (Table 16-9)
- Chlorobenzene (Table 16-10)

The locations of emissions sources for Table 16-4 are found by consulting Figure 16-2; those for Tables 16-2, 16-3, and 16-5 through 16-8 are found in Figure 16-1.

TABLE 16-5. CHARACTERIZATION OF EMISSIONS FROM THE METHYL ETHYL KETONE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Methyl ethyl ketone	scrubber-5	product	r	water	NA	NA	liquid	NA	NA
other VOC		by-products	r	water	NA	NA	liquid	NA	NA

Source: Hedley et al. 1975.

TABLE 16-6. CHARACTERIZATION OF EMISSIONS FROM THE ISOPROPYL ALCOHOL MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (refer to Figure 16-1)	Source	Type of Release	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
COD	product separation section-3	by-product	r	water	15-30	NA	liquid	NA	NA
Acetone	purification section-6	by-product	r	air	NA	NA	gas	NA	NA
diisopropyl alcohol		by-product	r	air	NA	NA	gas	NA	NA
diisopropyl ether		by-product	r	air	NA	NA	gas	NA	NA
isopropanol		by-product	r	air	NA	NA	gas	NA	NA
propane		by-product	r	air	NA	NA	gas	NA	NA
propylene		feed	r	air	NA	NA	gas	NA	NA

Source: Hedley et al. 1975. Based on 136,078 kkg/year capacity.

+Emissions are routine (r).

TABLE 16-7. CHARACTERIZATION OF EMISSIONS FROM THE SEC-BUTYL ALCOHOL MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (refer to Figure 16-1)	Source	Type of Release	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Butyl alcohol	distillation column-7	product	r	water	NA	NA	liquid	NA	NA
Sodium hydroxide		caustic	r	water	NA	NA	liquid	NA	NA
Sodium sulfate		caustic	r	water	NA	NA	liquid	NA	NA
Sulfuric acid	acid recovery section (not shown)	feedstock	r	water	NA	NA	liquid	NA	NA

Source: Hedley et al. 1975.

+Emissions are routine (r).

TABLE 16-8. CHARACTERIZATION OF EMISSIONS FROM THE ETHYL ALCOHOL MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location (refer to Figure 16-1)	Source	Type of Release	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
COD	product separation column-3	process bottoms	r	water	15-30	NA	liquid	NA	NA
Ethanol	product purification section-6	by-product	r	air	1.1	NA	gas	NA	NA
acetaldehyde		by-product	r	air	NA	NA	gas	NA	NA
di-ethyl ether		by-product	r	air	NA	NA	gas	NA	NA
ethylene		feed	r	air	NA	NA	gas	NA	NA
ethylene impurities		feed	r	air	NA	NA	gas	NA	NA

Source: Hedley et al. 1975. Based on 84,912 kkg/year capacity.

+Emissions are routine (r).

TABLE 16-9. CHARACTERIZATION OF EMISSIONS FROM THE PROPYLENE OXIDE MANUFACTURING PROCESS (CHLOROHYDRIN PROCESS)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release+	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Hydrocarbons	NA	feedstock impurities	r	NA	3.0^1	NA	NA	NA	NA
Chlorine	NA	feedstock	r	NA	.5^1	NA	NA	NA	NA
Dichloropropane	NA	by-product/feedstock	r	NA	7.0^1	NA	NA	NA	NA
Trichloropropane	NA	by-product/feedstock	r	NA	.5^1	NA	NA	NA	NA
Dichloropropanol	NA	by-product/feedstock	r	NA	.5^1	NA	NA	NA	NA
Epichlorohydrin	NA	by-product	r	NA	.10^1	NA	NA	NA	NA
Toluene	NA	feedstock/by-product	r	NA	.03^1	NA	NA	NA	NA
Ethyl benzene	NA	feedstock/by-product	r	NA	.01^1	NA	NA	NA	NA
Benzaldehyde	NA	by-product	r	NA	.005^1	NA	NA	NA	NA
Naphthalene	NA	feedstock/by-product	r	NA	.5^1	NA	NA	NA	NA
Ethane	NA	feedstock	r	air	8.5^1	NA	gas	NA	NA
Propylene oxide	scrubber vents & reactions	product	r	air	.75^2	NA	gas	NA	NA
	storage tanks		r	air	.031^2	NA	NA	NA	NA
	equipment leaks		a	air	.021^2	NA	NA	NA	NA

Sources:

[1] EPA, 1981, Organic Chemical Producers Data Base.
[2] SAI, Vol. II.
+Emissions are routine (r) or accidental (a).

TABLE 16-10. CHARACTERIZATION OF EMISSIONS FROM THE CHLOROBENZENE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release[+]	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Benzene	NA	by-product	r	water	12.2	NA	liquid	NA	NA
Chlorobenzene	NA	feedstock	r	water	NA	NA	liquid	NA	NA
Chlorotoluene	NA	feedstock/by-product	r	water	3.9	NA	liquid	NA	NA
Chlorotoluene	NA	feedstock/by-product	r	land	1.2	NA	solid	NA	NA
Dichlorobenzene	NA	feedstock/by-product	r	water	NA	NA	liquid	NA	NA
Diphenyl ether	NA	feedstock/by-product	r	land	.66	NA	solid	NA	NA
Ortho-dichlorobenzene	NA	feedstock/by-product	r	land	.60	NA	solid	NA	NA
Phenol	NA	product	r	water	.70	NA	liquid	NA	NA
Phenyl diphenyl ether	NA	by-product	r	land	19.3	NA	solid	NA	NA
Sodium chloride	NA	by-product	r	water	1559.0	NA	liquid	NA	NA

Source: EPA, 1981, Organic Chemical Producers Data Base.

[+] Emissions are routine (r).

REFERENCES

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals, 3rd Ed. New York: John Wiley and Sons, Inc.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Technomic Publishing Company, Inc. Westport, Connecticut.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Morrison, R. T., and R. N. Boyd. 1973. Organic Chemistry, 3rd Ed. Boston, Massachusetts: Allyn and Bacon, Inc.

SAI. 1981. Human Exposure to Atmospheric Concentrations of Selected Chemicals, Vol. II. Prepared for USEPA/OAQPS, Research Triangle Park, North Carolina.

SRI International. 1981. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

U.S. EPA. 1981. Organic Chemical Producers Data Base.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 9. U.S.Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028d.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 10. U.S.Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028e.

REFERENCES EVALUATED BUT NOT CITED

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides, and Explosives Industries. U.S.Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Kirk-Othmer. 1971. Encyclopedia of Chemical Technology. 3rd Ed. New York: John Wiley and Sons, Inc.

SECTION 17 - NITRATION

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SECTION 17

NITRATION

17.0 INTRODUCTION

Nitration is one of the most important means of introducing nitrogen into hydrocarbons. It occurs when one or more nitro groups ($-NO_2$) are introduced into organic compounds by the use of nitric acid. For aromatic compounds, nitration takes place in a nitric acid-sulfuric acid mixture with the sulfuric acid playing the role of a catalyst. An important point is that since nitric acid is also such a strong oxidizer, the reactor temperature must be kept low to avoid oxidation.

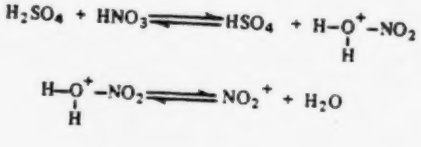
Figure 17-1 shows a typical nitration process sequence, the manufacture of nitrobenzene from nitric acid and benzene. Each process includes a stirred reactor, a spent acid purification train, and a product upgrading train. The principal organic chemicals manufactured by nitration are listed on Table 17-1.

17.1 GENERAL CHEMISTRY

Nitration is the unit process in which nitrogen is introduced into hydrocarbon by the use of nitric acid. For aromatic compounds, a typical nitration process may be expressed as follows:

$$R.H + HNO_3 \xrightarrow{H_2SO_4} R.NO_2 + H_2O \qquad AH = -15.0 \text{ to } 35.0 \text{ kcal}$$

This is an electrophilic reaction in which the electrophilic agent is the nitronium ion, NO_2^+. The sulfuric acid protonates the nitric acid to give $H_2NO_3^+$, which loses water to form NO_2^+:



$$H_2SO_4 + HNO_3 \rightleftharpoons HSO_4 + H-\underset{H}{O^+}-NO_2$$

$$H-\underset{H}{O^+}-NO_2 \rightleftharpoons NO_2^+ + H_2O$$

FIGURE 17-1. A TYPICAL NITRATION PROCESS: MANUFACTURE OF NITRO-BENZENE FROM BENZENE AND NITRIC ACID

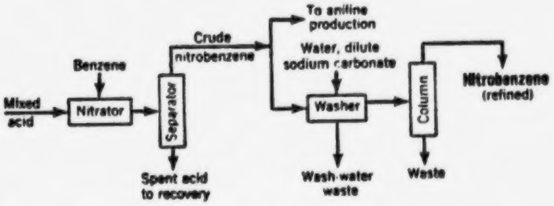


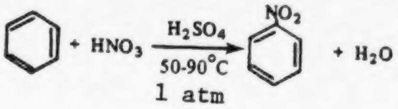
TABLE 17-1. NITRATION PRODUCTS[1] AND THEIR MANUFACTURE IN 1980[2]

Product	Amount kkg	Feedstock	Other Required Processes
o-Aminophenol	NA[3]	Phenol	Amination by reduction
4,6-Dinitro-o-cresol	NA[3]	Cresol	None
2,4-Dinitrophenol	NA[3]	Phenol	None
2,4-Dinitrotoluene	NA[3]	Toluene	None
2,4-(and 2,6)			
Dinitrotoluene	NA[3]	Toluene	None
Nitrobenzene	610,176	Benzene	None
o-Nitrophenol	NA[3]	Phenol	None
p-Nitrophenol	29,056	Phenol	None
∿-Nitrophenol	NA[3]	Toluene	None
o-Nitrotoluene	NA[3]	Toluene	None
p-Nitrotoluene	NA[3]	Toluene	None
Toluene diisocyanate (TDI)	259,688	Phosgene	Hydrogenation
(80/20 2,4=2,6-TDI)		Toluene	Phosgenation

Source: 1. Herrick et al. 1979a.
2. SRI 1981. Production levels are assumed to be 80% of plant nameplate capacity. It may not be assumed, however, that the products are solely manufactured by a nitration process.
3. SRI 1981. No quantitative data are available. However, a list of manufacturers is provided.

Removal of the water favors the nitration reaction by shifting the equilibrium to the right. The presence of sulfuric acid effects this removal.

An example of a nitration reaction is the manufacture of nitrobenzene from benzene:



17.2 DESCRIPTION OF DISCHARGES

Emissions from a typical nitration process are released to the three media of air, land, and water at different stages in the process:

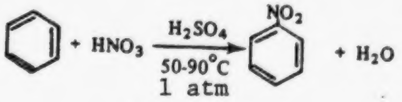
Reactor	-	Volatile organic emissions, nitrogen oxide emissions, and sulfuric acid fumes.
Washer/Neutralizer	-	Nitrobenzene, nitrated phenols, sodium sulfate, and sodium carbonate combined in the wastewaters; purges of volatile organics.
Sulfuric acid regeneration train	-	Purges of nitrogen oxide, sulfuric acid fumes, and volatile organics.
Product Upgrading	-	Purges of volatile organics from condensers; possibility of nitro-substituted aromatic compounds in the heavy ends.
Storage Vessels	-	Storage of feedstock and product result in volatile organic compounds emissions.
Fugitive Emissions	-	Occur from valves, flanges, pump seals, compressor seals, presure relief valves, drain, and cooling towers.
Secondary Emissions	-	Occur from the handling and disposal of process waste liquid.

17.3 DESCRIPTION OF AN EXAMPLE PRODUCTION PROCESS: MANUFACTURE OF NITROBENZENE BY THE NITRATION OF BENZENE

This description of the manufacture of nitrobenzene by the nitration of benzene consists of three major steps: 1) nitration reaction and subsequent product separation, 2) nitrobenzene upgrading, and 3) spent acid recovery. Figure 17-2 illustrates a typical continuous process and the location of possible emission points. For each part, the description highlights the emissions associated with this step of the process.

17.3.1 Nitration Reaction and Subsequent Product Separation

As has been previously noted in Section 17.1, the nitration reaction is as follows:



ΔH = 27.0 kcal
95-98% yield

Figure 17-2. is a process flow diagram for the manufacture of nitrobenzene. The reactor vessel, or nitrator, is a specially built cast-iron or steel kettle fitted with a high speed (600 rpm) agitator and a helical cooling coil. It is so designed to keep the reaction temperatures as low as possible and avoid nitric acid acting as an oxidizing agent.

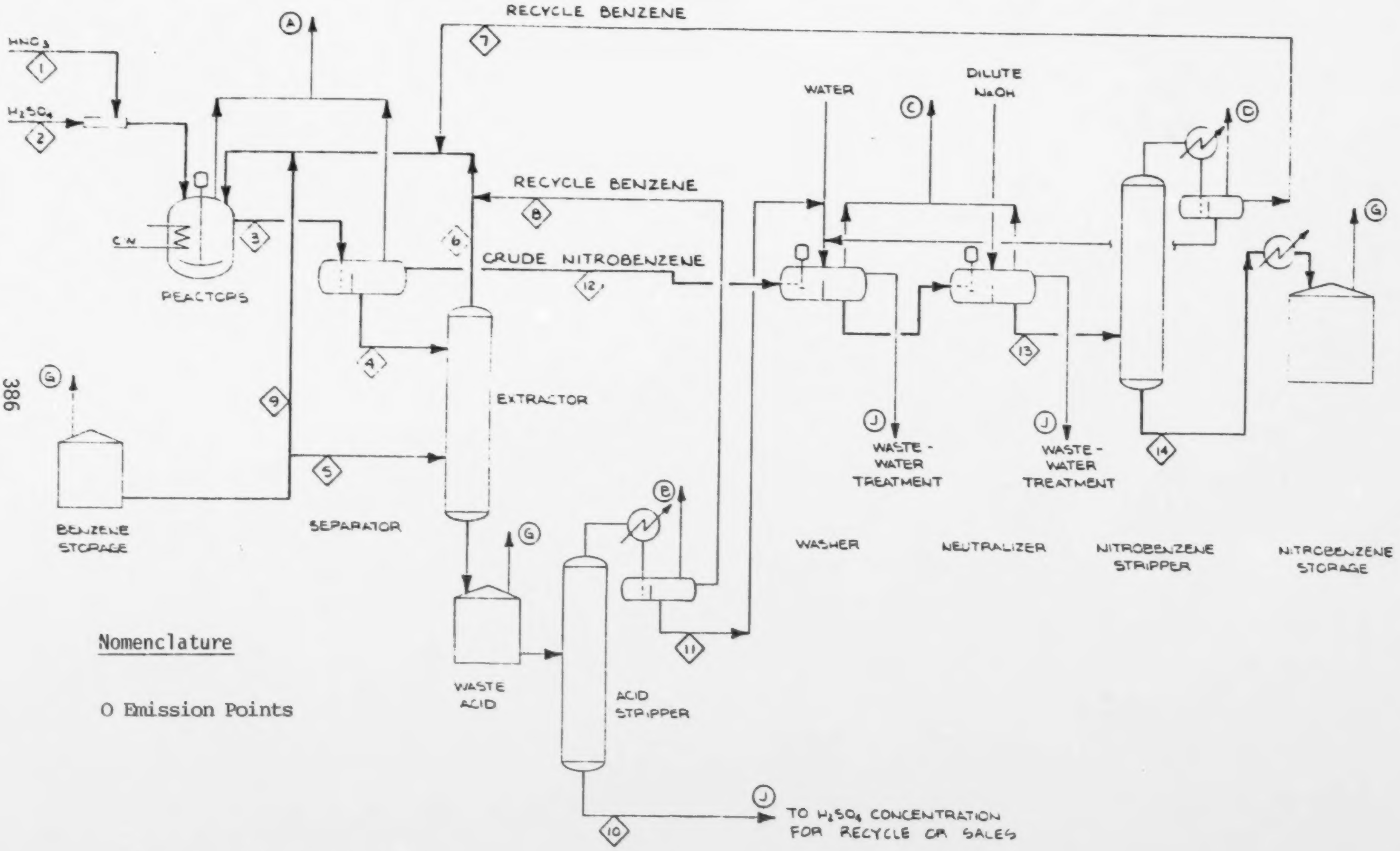
The feed material requirements per kkg of nitrobenzene produced are as follows (Faith et al. 1965; Shreve 1967):

	Benzene	590 kg.
Mixed Acid	Sulfuric	655 kg.
	Nitric	481 kg.
	Water	99 kg.
	Sodium Carbonate	9 kg.

Reactor residence time is temperature dependent and for continuous manufacturing processes ranges from fifteen to twenty minutes (Faith et al. 1965).

The crude reaction mixture flows to a separator where the organic phase (principally composed of nitrobenzene) is decanted from the aqueous waste acid. Residence time in the separator varies from 10 to 20 minutes.

FIGURE 17-2. PROCESS FLOW DIAGRAM FOR MANUFACTURE OF NITROBENZENE



Nomenclature

O Emission Points

Source: White 1980, Vol. 7

17.3.1.1 Emissions

Benzene and nitrogen oxide emissions are vented through an absorber associated with the reactor and also from the separator vent. Some organic by-products, primarily nitrated phenols, are formed in the reactor; typically, these phenolic materials are discharged with the wastewater effluent.

17.3.2 Nitrobenzene Upgrading

Crude nitrobenzene from the separator is washed first with water and then with dilute sodium carbonate to remove acids and organic impurities such as the nitrophenols. The washing takes place in tanks of similar size and appearance to the nitrator with high-speed mechanical agitation; washing is completed in 10 minutes (Faith et al. 1965). The aqueous washer and neutralizer streams are sent for wastewater treatment while the organic layer is sent to a nitrobenzene stripping column.

In the nitrobenzene column, water and most of the low boiling hydrocarbon based compounds are carried in the overhead stream which is subsequently condensed into a benzene phase (that is sent back to the reactor) and an aqueous phase (that is sent to the washer). A lower stream (that consists of nitrobenzene) is cooled and sent to storage.

17.3.2.1 Emissions

As mentioned previously, the aqueous washer and neutralizer streams contain impurities such as the nitrophenols, some nitrobenzene, sodium sulfate, and residual sodium carbonate (Gruber 1975, White 1980). The wastestream from the nitrobenzene column contains nitrobody heavy ends (unknown nitro substituted aromatic compounds).

Some benzene and other volatile organic compounds are vented from the washer vessels and also from the condenser associated with the nitrobenzene stripping column.

17.3.3 Spent Acid Recovery

The acid phase stream from the separator is contacted in the extractor with fresh benzene from storage to extract most of the nitrobenzene and nitric acid. The extracted acid phase stream is subsequently sent to a stripper where water and benzene are carried in the overhead stream with separation into a benzene phase (that is recycled to the reactor) and an aqueous phase (that is sent to the washer).

The sulfuric acid is then concentrated and recycled back to the reactor.

17.3.3.1 Emissions

Benzene and other volatile organic compounds are vented from the separator associated with the spent acid stripper. Some of the sulfuric acid is lost irrevocably in the concentrator.

17.3.4 Other Issues

Many of the processes are padded with nitrogen gas to reduce explosion and fire hazards.

17.3.4.1 Emissions

The purge gases from process units such as the separator associated with the nitrator, the condensers associated with the acid and nitrobenzene stripping columns, and the washer and neutralizer contain nitrogen.

Leaks in valves, pump seals, and other equipment can be sources of fugitive emissions of benzene, nitrobenzene, and other volatile organic compounds (VOC's). Leaks can also occur from corrosion by the nitric and sulfuric acids.

Storage emissions can occur from tanks storing benzene, nitrobenzene, and the mineral acids.

17.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the following manufacturing processes:

- Nitrobenzene (consult Table 17-2 in conjunction with Figure 17-2)
- TDI-Nitration Train (consult Table 17-3)

No emissions data have been found for any other nitration manufacturing process.

TABLE 17-2. CHARACTERIZATION OF EMISSIONS FROM THE NITROBENZENE MANUFACTURING PROCESS

Pollutant	Location (Refer to Figure 17-1)	Source	Type of Release[+]	Receiving Medium	Uncontrolled Emissions		Form	Controlled Emissions	
					quantity kg/kkg product	rate kg/hr		control technology	quantity kg/kkg product
	Nitrator/Separator Vent								
Nitrogen oxide	generated by side reactions	by-product	r	air	0.09[1]	NA	gas	NA	NA
Benzene		feed	r	air	0.96[2]-7.5[1]	9.86[2]	gas	see note 4	NA
Total VOC[7]	includes all other volatile organics	feed/by-product	r	air	0.965[2]	9.91[2]	gas	see note 4	NA
	Washer/Neutralizer								
Benzene		feed	r	air	0.0081[2]	0.0832[2]	gas	see note 4	NA
Total VOC		feed/by-product	r	air	0.0107[2]	0.110[2]	gas	see note 4	NA
Nitrobenzene	contained in the aqueous waste and neutralizer streams	product	r	water	0.004[3]	NA	liquid	NA	NA
Nitrated phenols		by-product	r	water	2.0[2]	NA	liquid	NA	NA
Sodium sulfate		by-product	r	water	NA[3]	NA	liquid	NA	NA
Sodium carbonate		feed	r	water	NA[3]	NA	liquid	NA	NA
	Nitrobenzene Stripper								
Benzene		feed	r	air	0.17[2]	1.75[2]	gas	see note 4	NA
Total VOC		feed/by-product	r	air	0.171[2]	1.76[2]	gas	see note 4	NA
Nitro-substituted Aromatic compounds	contained in the heavy ends	by-product	r	land	NA[3]	NA	solid	NA	NA
	Spent-Acid Stripper								
Benzene		feed	r	air	0.17[2]	1.75[2]	gas	thermal oxidizer	0.0144[4]
Total VOC		feed/by-product	r	air	0.171[2]	1.76[2]	gas	thermal oxidizer	0.0144
Nitrogen oxides		by-product	r	air	0.16[1]	NA	gas	NA	NA
	Storage Vessels								
Benzene	benzene storage	feed	r	air	0.283[2]	2.91[2]	gas	floating roof	0.044
Total VOC	nitrobenzene storage	product	r	air	0.0019[2]	0.0197[2]	gas	none	0.0019
	Miscellaneous								
Benzene	fugitive emissions	feed	r	air	0.38[5]-1.9[5]	6.5[5]	gas	detect,correct leaks	0.099[5]-0.5[5]
VOC	fugitive emissions	feed/by-product	r	air	0.6[5]-3.0[5]	10.2[5]	gas	mechanical seals	0.216[5]-1.08[5]
Sulfuric acid	lost in wastewater stream	feed	r	water	10.0[6]-20.0[6]	NA	liquid	NA	NA

TABLE 17-2. CHARACTERIZATION OF EMISSIONS FROM THE NITROBENZENE MANUFACTURING PROCESS (CONTINUED)

Pollutant	Location	Source	Type of Release	Receiving Medium	Uncontrolled Emissions		Form	Controlled Emissions	
					quantity kg/kkg product	rate kg/hr		control technology	quantity kg/kkg product
	Secondary								
Benzene 0.10	handling/disposal of process liquids	feed	r	air	0.10^2	1.03^2	gas	none	
VOC 0.33	from spent acid stripper, washer/neutralizer	feed/by-product	r	air	0.33^2	3.39^2	gas	none	

---

[1] Source: Hedley 1975, p. 217.

[2] Source: White 1980, Volume 7. Data based on a model state-of-the-art plant capacity of 90,000 kkg/yr.

[3] Source: Gruber 1975, pps. 5-6 to 5-8.

[4] Source: White 1980, Volume 7, p. V-2. It is assumed that the vent emissions from the nitrator/separator, the spent acid stripper condenser, the washer and neutralizer, the nitrobenzene stripper, plus a small (1-day) supply of benzene storage vessel plus the waste-acid storage vessel, are combined and thermally oxidized.

[5] Source: White 1980, Volume 7. Process pumps and valves are considered sources of fugitive emissions. Each model plant is estimated to have 42 pumps (including 17 spares), 500 process valves, and 20 pressure-relief valves. All pumps have mechanical seals. It is assumed that 25 percent of the pumps and valves are being used in benzene service.

[6] Source: Faith et al. 1965.

[7] VOC denotes volatile organic compounds.

+Denotes that release is routine (r) or accidental (a).

TABLE 17-3. CHARACTERIZATION OF EMISSIONS FROM THE TOLUENE DIISOCYANATE (TDI) MANUFACTURING PROCESS - NITRATION TRAIN

Pollutant	Location	Source	Type of Release	Receiving Medium	Uncontrolled Emissions		Form	Controlled Emissions	
					quantity kg/kkg product	rate kg/hr		control technology	quantity kg/kkg product
VOC[2]	nitration reactor	by-product	r	air	0.025	25.9	gas	wear scrubber (for H_2SO_4 removal)	.01
Nitroaromatics	H_2SO_4 concentration unit	by-product	r	air	5.0	0.13	gas	wet remover	2
SO_2		by-product	r	air	0.03	NA	gas	scrubber (for H_2SO_4 removal)	NA
NO_x			r	air	2.0	NA	gas		NA
H_2SO_4 vapor			r	air	12.0	NA	gas		NA

[1] kg of pollutant per kkg of TDI produced

[2] VOC = volatile organic compounds

[3] Source: White 1980, Volume 7, based on 45,000 kkg/yr capacity.

+Indicates that a release is routine (r).

REFERENCES

Faith, W. L. D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals. 3rd ed. New York: John Wiley and Sons, Inc.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. U.S.Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Co., Inc.

Herrick, E. C., J. A. King, R. P. Ouellette, and P. N. Cheremisinoff. 1979. Unit Process Guide to Organic Chemical Industries. AnnArbor, Michigan: Ann Arbor Science Publishers, Inc.

Shreve, R. N. 1967. Chemical Process Industries, 3rd ed. New York, New York: McGraw-Hill Book Company.

Solomons, T. W. Graham. 1978. Organic Chemistry, John Wiley, New York. p. 464-468.

SRI International. 1981. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

Wetherold, R. G., D. D. Rosebrook, and B. A. Tichenor. 1981. Assessment of Atmospheric Emissions from Petroleum Refining. Research Triangle Park, North Carolina: U.S. Environmental Protection Agency.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 7. U.S.Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, N. C. EPA-450/3-80-028b.

REFERENCES EVALUATED BUT NOT USED

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

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SECTION 18

OXIDATION

18.0 INTRODUCTION

The unit process of oxidation is the chemical reaction of organic compounds with oxygen to introduce one or more oxygen atoms into the compound, and/or to remove hydrogen atoms from the compound. Most oxidation processes use a catalyst (cupric chloride, palladium chloride, silver, metal oxide, molybdenum, cobalt, iron, and cupric nitrate).

The oxidation processes are similar. Each process includes a reactor and some heat transfer method. Most oxidation reactions are highly exothermic, and oxidation equipment must provide efficient heat transfer. Each process also includes a separation and purification method. Figures 18-1a and 18-1b are typical process diagrams for liquid phase and vapor phase oxidation processes respectively. The principal organic chemicals manufactured by oxidation are listed in Table 18-1.

18.1 GENERAL CHEMISTRY

Oxidation is one of the most useful chemical conversions for the entire organic technology. The reaction possibiities of oxidation are so varied that a type reaction is impossible. Generally, oxidation involves splitting of C-C and C-H bonds with formation of C-O bonds. The cheapest reagent is air, but more and more oxygen is being used. Oxygen can be more economical than air, because of enhanced yields, reduced recycle intervals, higher reaction rates, reduced equipment sizes, and reduced heat loss to nitrogen.

Oxidation reactions are carried out in both the liquid and vapor phases, using a variety of catalysts. The reactions are highly exothermic, and the problem of heat removal is a difficult one. Below are three examples of oxidation.

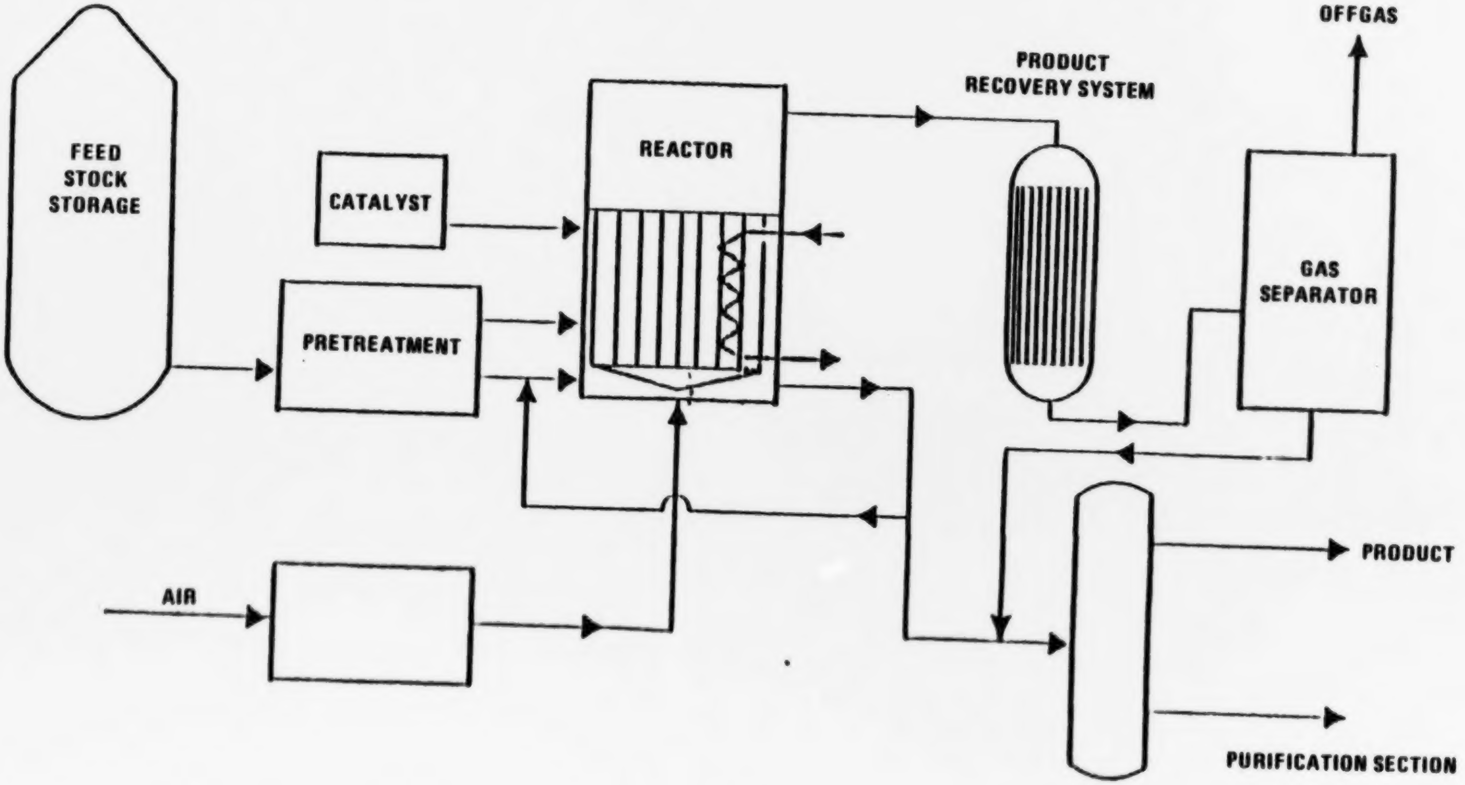


FIGURE 18 - 1a. SCHEMATIC OF A FLOWSHEET FOR A LIQUID PHASE AIR OXIDATION PROCESS

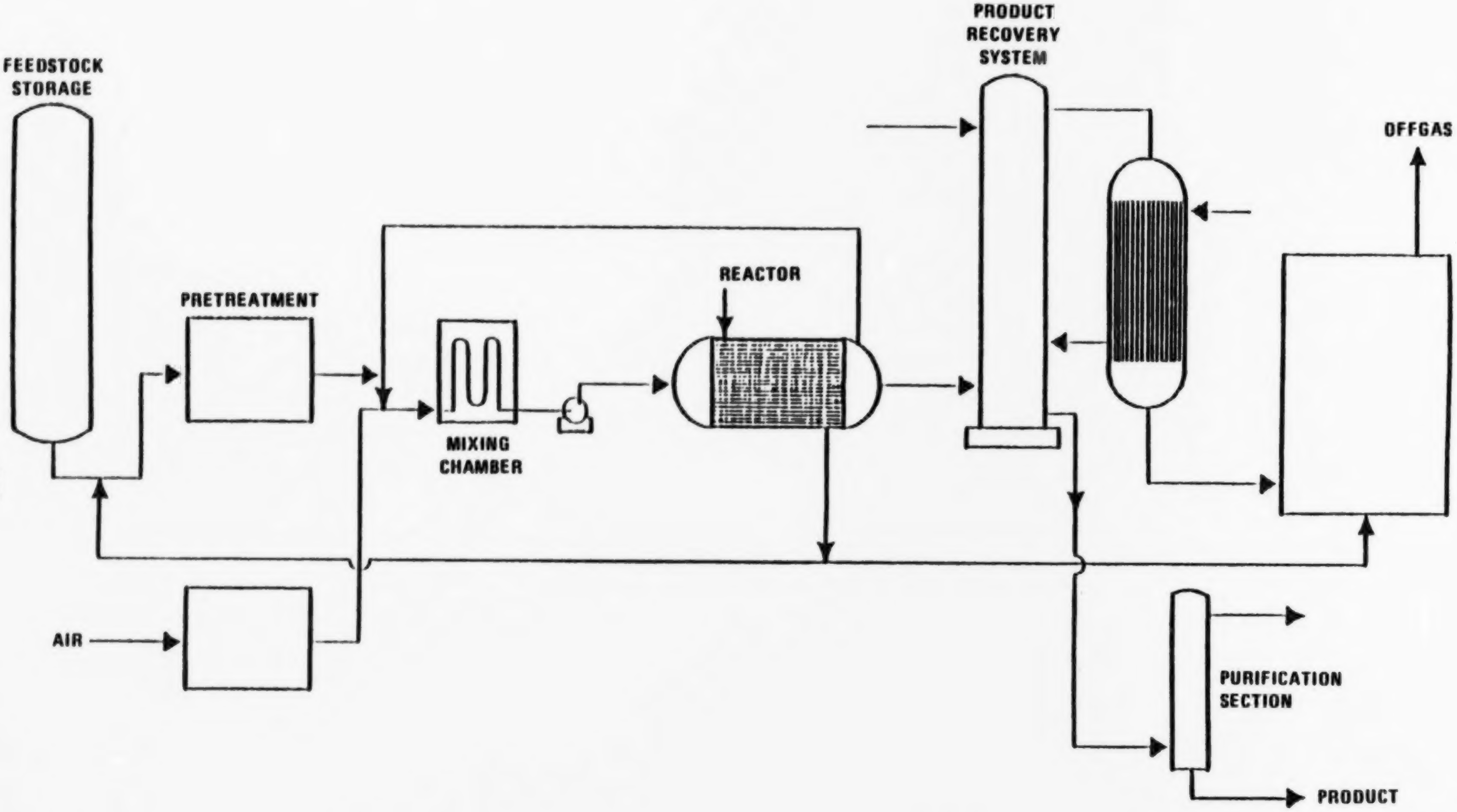


FIGURE 18 - 1b. SCHEMATIC OF A FLOWHSEET FOR A VAPOR PHASE AIR OXIDATION PROCESS

TABLE 18-1. OXIDATION PRODUCTS AND THEIR PRODUCTION IN 1979

Product*	Amount kkg	Feedstock	Other Required Processes
Acetaldehyde	479,906[1]	ethylene	none
Acetic acid	1,481,044	n-butenes	alkylation
Acetic acid	1,481,044	light naphtha	none
Acetic acid Peracetic acid	1,481,044 NA	acetaldehyde	none
Acetic acid Terephthalic acid	1,481,044 NA	n-butane p-xylene	none
Acetone Phenol	478,091[1] 36,553	benzene propylene	none
Acetylene Ethylene	NA NA	hydrocarbons (C_1-C_8)	cracking
Acrolein Acrylic acid Acetaldehyde	NA 275,788 NA	propylene	none
Acrylic acid Acrylic esters	328,720[2]	propylene alcohols	esterification
Adipic acid	682,160[3]	cyclohexane	none
Adipic acid	682,160[3]	cyclohexyl alcohol	none
Anthraquinone	18,897[1]	anthracene	none
Benzoic acid	34,946	toluene	none
Tert-butyl alcohol	NA	isobutane	none
Caprolactam	428,828	cyclohexane	Beckmann rearrangement oxidation
Caprolactam	428,828	toluene	acid rearrangement hydrogenation
Cyclohexanone Cyclohexyl alcohol	739,200[4]	cyclohexane	none

TABLE 18-1. OXIDATION PRODUCTS AND THEIR PRODUCTION IN 1979 (continued)

Product*	Amount kkg	Feedstock	Other Required Processes
Dimethyl terephthalate	653,600[3]	methanol p-xylene	esterification
Ethyl acrylate	143,328	ethyl alcohol propylene	esterification
Ethylene oxide	8,618[5]	ethylene	none
Ethylene oxide/ ethylene glycol	8,618[5]/2,144,866	ethylene	hydrolysis
Formaldehyde	2,708,479	methanol with silver catalyst	none
Formaldehyde	2,708,479	methanol with metal oxide catalyst	none
Formaldehyde	NA	dimethyl ether	none
Formic acid	8,165[5]	light hydrocarbons	none
Fumaric acid (trans-1,2-ethylene dicarboxylic acid)	23,078	benzene	isomerization
Glycerine	47,200[6]	propylene	none
Isophthalic acid	NA	m-xylene	none
Maleic anhydride	146,614	butadiene (and other C_4 hydrocarbons)	none
Maleic anhydride	146,614	benzene	none
Maleic anhydride	146,614	butene-1, butene-2, butadiene (if present)	none
Methyl methacrylate	422,241	isobutylene, methanol	esterification
Pelargonic acid Caproic acid Azeliac acid	NA NA NA	oils (tall, red, soybean)	ozonolysis
Pelargonic acid Undecanoic acid Tridecanoic acid	NA NA NA	α-olefins	ozonolysis

TABLE 18-1. OXIDATION PRODUCTS AND THEIR PRODUCTION IN 1979 (continued)

Product*	Amount kkg	Feedstock	Other Required Processes
Phenol Acetone	1,315,715 782,254	cumene	acid cleavage
Phenol Acetone	36,553 NA	benzene, propylene	acid cleavage alkylation
Phenol Hydrogen	36,553 NA	cyclohexane	dehydrogenation
Phthalic anhydride	215,459[5]	naphthalene	none
Phthalic anhydride	215,459[5]	o-xylene	alkylation
Phthalic dianhydride (1,2,4,5-benzenetetracarboxylic-1,2,4,5-dianhydride)	NA	pseudocumene	alkylation
Suberic acid Dodecanoic acid	NA NA	cyclic olefins	ozonolysis
Terephthalic acid	1,051,200[3]	p-xylene	none
Tetrahydrofuran, 2,3,4,5-tetracarboxylic dianhydride	NA NA	furan maleic anydride	condensation
Tetramethylthiuram disulfide (thiuram) [bis(dimethylthiocarbamoyl)disulfide]	NA	ammonia, carbon disulfide, dimethylamine, hydrogen peroxide	condensation
Trimellitic anhydride (1,2,4-benzene-tricarboxylic acid, 1,2-anhydride)	NA	pseudocumene	none

Sources: Hedley, et al. 1979; Synthetic Organic Chemicals 1980.

Note: Oxidation is not always the major method of production of these chemicals.

*Some oxidation processes have more than one product.

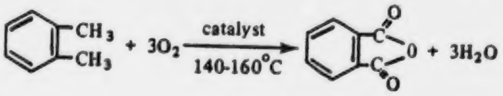
[1] Shreve 1967, production in 1964.
[2] White 1980, 80% of 1976 capacity of both products.
[3] White 1980, 80% of 1978 capacity.
[4] White 1980, 80% of 1979 capacity of both products.
[5] Faith 1965, production in 1963.
[6] White 1980, 80% of 1977 capacity.

The oxidation process for acetaldehyde production by the direct oxidation of ethylene using a catalyst solution of cupric chloride and of palladium chloride may be summarized as follows:

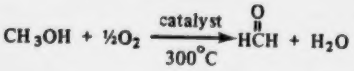
$$CH_2{=}CH_2 + 2CuCl_2 + H_2O \xrightarrow{PdCl_2} CH_3CHO + 2CuCl + 2HCl$$

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O$$

Oxidation of an aromatic compound is illustrated by the production of phthalic anhydride from o-xylene. Air at 1.5 to 2 atm pressure is heated to 140 to 160°C, mixed with vaporized o-xylene, and passed over a proprietary granular catalyst. The equation for the reaction follows:



An example of oxidation in which the oxygen atom is already present in the molecule and in which oxidation consists of removal of the hydrogen atom is the synthesis of formaldehyde from methanol. A mixture of methanol in air is sent to a reactor filled with metallic silver catalyst or ferromolybdenum oxide maintained at 300°C. The equation for the reaction is as follows:



$$CH_3OH + \tfrac{1}{2}O_2 \xrightarrow[300^\circ C]{catalyst} H\overset{O}{\overset{\|}{C}}H + H_2O$$

18.2 DESCRIPTION OF DISCHARGES

Releases from a typical oxidation process occur as fugitive gaseous emissions, as vent gases, in wastewater, and as catalyst residue.

Fugitive - occur from process valves, process pump seals, relief valves, compressor seals, drains, and cooling towers.

Process - occur from reactor off-gases.

Separation and purification - occur from scrubber vents, scrubber wastewater, and distillation vents.

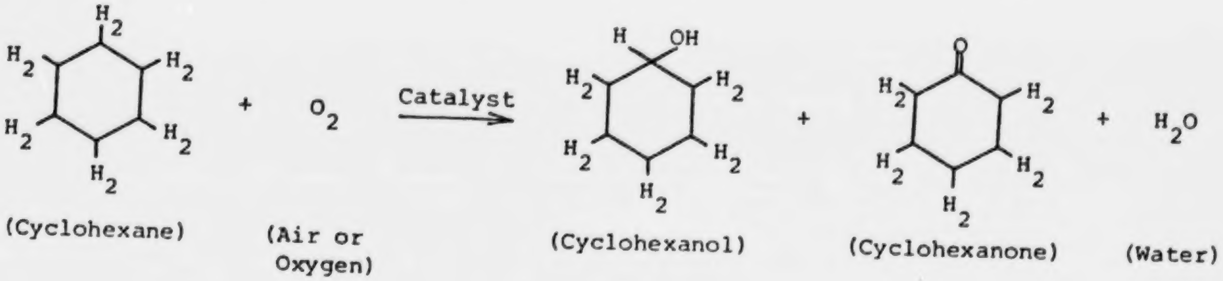
Storage - occur from feed, intermediate, and product storage.

Handling - occur from transfer of organics.

Secondary - occur from catalyst residue.

18.3 PRODUCTION OF CYCLOHEXANOL AND CYCLOHEXANONE BY OXIDATION OF CYCLOHEXANE AND RESULTING EMISSIONS

The reaction for the cyclohexane oxidation process is as follows:



The following discussion is based on information in IT Enviroscience (1980) and is divided into four subsections: (1) reaction process, (2) separation and purification, (3) separation and purification emissions, and (4) fugitive, handling, storage, and secondary emissions. Figure 18-2 is a flow diagram illustrating a model plant for the manufacture of cyclohexanol/cyclohexanone (ketone-alcohol or KA oil) by cyclohexane oxidation.

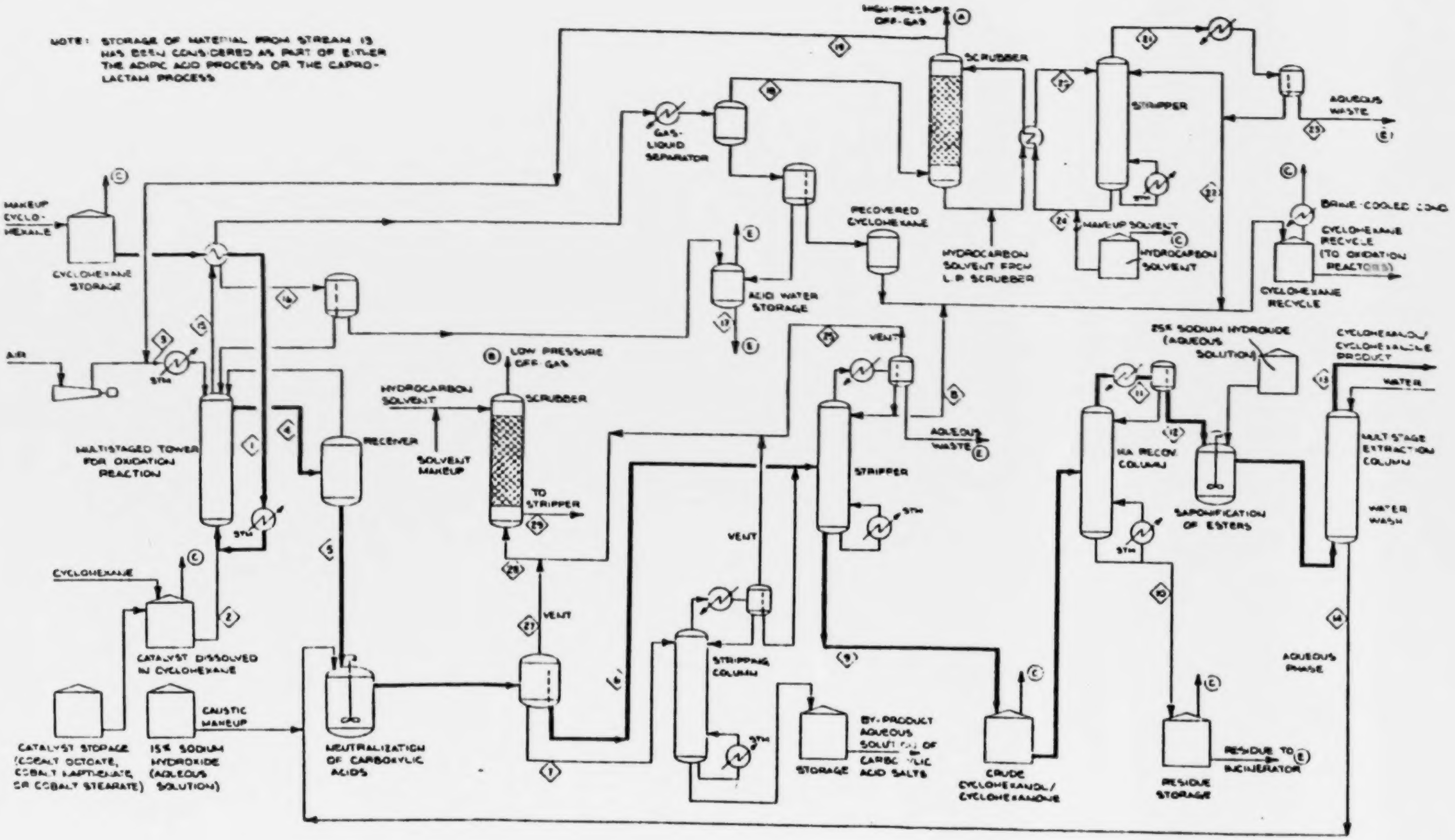
18.3.1 Reaction Process

Production of cyclohexanol/cyclohexanone begins in the oxidation reactor. Cyclohexane (Stream 1) is preheated and combined with the catalyst (Stream 2) before it enters the multistage oxidation tower reactor. Compressed air is preheated and fed to the reactor (Stream 3). KA oil product from the reactor (Stream 4) is collected in a receiver.

18.3.2 Separation and Purification

The product (Stream 5) then enters a neutralization reactor where carboxylic acid by-products are neutralized. The KA oil product and the aqueous phase containing carboxylic acid salts enter a phase separator. KA oil product (Stream 6) is sent to a stripping column for removal of

FIGURE 18-2. PROCESS FLOW DIAGRAM FOR UNCONTROLLED MODEL PLANT PRODUCING CYCLOHEXANOL/CYCLOHEXANONE BY CYCLOHEXANE OXIDATION


NOTE: STORAGE OF MATERIAL FROM STREAM 13 HAS BEEN CONSIDERED AS PART OF EITHER THE ADIPIC ACID PROCESS OR THE CAPROLACTAM PROCESS
MAKEUP CYCLOHEXANE
CYCLOHEXANE STORAGE
AIR
STM
MULTISTAGED TOWER FOR OXIDATION REACTION
CYCLOHEXANE
CATALYST DISSOLVED IN CYCLOHEXANE
CATALYST STORAGE (COBALT OCTOATE, COBALT NAPTHENATE, OR COBALT STEARATE)
15% SODIUM HYDROXIDE (AQUEOUS SOLUTION)
CAUSTIC MAKEUP
RECEIVER
NEUTRALIZATION OF CARBOXYLIC ACIDS
GAS-LIQUID SEPARATOR
ACID WATER STORAGE
LOW PRESSURE OFF GAS
HYDROCARBON SOLVENT
SOLVENT MAKEUP
SCRUBBER
TO STRIPPER
VENT
HIGH-PRESSURE OFF-GAS
RECOVERED CYCLOHEXANE
HYDROCARBON SOLVENT FROM L.P. SCRUBBER
STRIPPER
MAKEUP SOLVENT
HYDROCARBON SOLVENT
AQUEOUS WASTE
BRINE-COOLED COND
CYCLOHEXANE RECYCLE (TO OXIDATION REACTORS)
CYCLOHEXANE RECYCLE
AQUEOUS WASTE
STRIPPING COLUMN
STORAGE
BY-PRODUCT AQUEOUS SOLUTION OF CARBOXYLIC ACID SALTS
CRUDE CYCLOHEXANOL/CYCLOHEXANONE
HA RECOV COLUMN
25% SODIUM HYDROXIDE (AQUEOUS SOLUTION)
SAPONIFICATION OF ESTERS
CYCLOHEXANOL/CYCLOHEXANONE PRODUCT
WATER
MULT STAGE EXTRACTION COLUMN
WATER WASH
AQUEOUS PHASE
RESIDUE STORAGE
RESIDUE TO INCINERATOR
A
B
C
E
1
2
3
4
5
6
7
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29

Source: White 1980.

Reproduced from best available copy.

cyclohexane. The aqueous phase (Stream 7) is stripped of organics prior to storage and is either sold or thermally oxidized.

Recovered cyclohexane (Stream 8) from the stripping column is recycled for another pass through the oxidation reactor. KA oil product (Stream 9) from the bottom of the stripping column enters a KA oil recovery column. Residue from the KA recovery column (Stream 10) is thermally oxidized. Overhead product from the column (Stream 11) goes to a phase separator. The oil phase (Stream 12) is removed and then sent to a reactor for saponification of cyclohexyl esters with caustic. The caustic is removed from the KA oil product by a water wash. Crude KA oil product (Stream 13) is removed form the extraction column. Depending on the end use, the product may be further purified or be used directly as a reactant in another process. The aqueous phase (Stream 14) from the extraction column is recycled to the neutralization reactor.

Off-gas vented from the cyclohexane oxidation reactor (Stream 15) is cross-exchanged with cyclohexane feed for heat recovery transfer. Organics condensing from the gas stream (Stream 16) enter a phase separator, where the oil phase is separated and recycled to the reactor. The aqueous phase is combined with other aqueous waste (acid water storage) and leaves the system (Stream E). After the heat exchanger, the off-gas from the cyclohexane oxidation reactor goes to a gas-liquid separator. Nitrogen and other gases (Stream 18) leaving the gas-liquid separator pass through a scrubber for additional cyclohexane recovery. Part of the high-pressure off-gas leaving the scrubber is recycled as diluent to compressed air supplied to the cyclohexane oxidation reactor (Stream 19); the remainder is vented (Vent A). Cyclohexane and make-up adsorption solvent (Stream 20) enter a stripper for removal of cyclohexane and water as overhead product (Stream 21). This overhead product enters a phase separator for separation of the cyclohexane, which is then recycled to the system (Stream 22). The aqueous phase leaves the system as an aqueous waste stream (Stream 23). Bottoms from the stripping column (Stream 24) are recycled to the scrubber.

Off-gas from the phase separators (Streams 25, 26, and 27) is combined and is sent to a scrubber for removal of cyclohexane (Stream 28). The low-pressure off-gas is discharged (Vent B). Hydrocarbon solvent, containing cyclohexane, is sent to a stripper for cyclohexane recovery (Stream 29).

18.3.2.1 Separation and Purification Emissions

Process emissions occur from the high-pressure and low-pressure scrubber vents (Vents A and B) and the stripper wastewater. Emissions from Vents A and B consist of VOC and carbon monoxide. All cyclohexane oxidation plants are equipped with high- and low-pressure scrubbers, which are used mainly for economic reasons to recover hydrocarbons and are an integral part of the process. Emissions from wastewater consist of organic sodium salts and sodium hydroxide.

18.3.3 Fugitive, Handling, Storage, and Secondary Emissions

Fugitive emissions occur from process pumps, process valves, and pressure relief valves handling VOC. Virtually no handling emissions result from cyclohexanol/cyclohexanone since it is used captively. There are some emissions from storage of cyclohexane, cyclohexanol/cyclohexanone, hydrocarbon solvent, and process residue.

Secondary VOC emissions can occur from aqueous wastewater effluent and from storage and thermal oxidation of residue resulting from KA oil recovery still (Stream 10).

18.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided in Table 18-2 for the following manufacturing processes:

- acetic acid, peracetic acid
- acrolein, acrylic acid, acetaldehyde
- acrylic acid, acrylic ester (consult Figure 18-3)
- adipic acid from cyclohexane (consult Figure 18-4)

- adipic acid from cyclohexyl alcohol (consult Figure 18-5)
- cyclohexanone, cyclohexyl alcohol (consult Figure 18-2)
- ethylene oxide
- ethylene oxide, ethylene glycol
- formaldehyde from methanol with metallic silver catalyst
- glycerin (consult Figure 18-6)
- isophthalic acid
- maleic anhydride from benzene (consult Figure 18-7)
- phenol, acetone from cumene (consult Figures 18-8 and 18-9)
- phthalic anhydride from naphthalene
- phthalic anhydride from o-xylene
- terephthalic acid

No emissions data have been found for any other oxidation manufacturing processes.

TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES

						Uncontrolled Emissions			Controlled Emissions		
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product	Stream Design.
Acetaldehyde	acetic acid	distillation bottoms	by-product	r	water	13.9^{4}	NA	liquid	NA	NA	
	acetyl chloride		by-product	r	water	4.2^{4}	NA	liquid	NA	NA	
	chloral		by-product	r	water	2.1^{4}	NA	liquid	NA	NA	
	paraldehyde		by-product	r	water	1.6^{4}	NA	liquid	NA	NA	
	Other organics (including chloroform, formaldehyde, and methylene and methyl chloride)		by-product	r	water	4.0^{4}	NA	liquid	NA	NA	
	acetaldehyde	distillation side-cut	product	r	water	7.8^{4}	NA	liquid	NA	NA	
	acetic acid		by-product	r	water	0.6^{4}	NA	liquid	NA	NA	
	chloroacetaldehyde		by-product	r	water	5.5^{4}	NA	liquid	NA	NA	
	acetyl chloride		by-product	r	water	5.0^{4}	NA	liquid	NA	NA	
	chloral		by-product	r	water	3.4^{4}	NA	liquid	NA	NA	
	other organics (including chloroform, formaldehyde, and methylene and methyl chloride)		by-product	r	water	2.0^{4}	NA	liquid	NA	NA	
Acetic acid Peracetic acid	VOC emissions	process	NA	r	air	13.5^{5}	320^{5}	gas	NA	NA	
	methane	scrubber vent	by-product	r	air	1.8^{2}	NA	gas	NA	NA	
	carbon monoxide	scrubber vent	by-product	r	air	3.25^{2}	NA	gas	NA	NA	
	organics	waste flow from system	feed, by-product	r	water	64.1^{2}	NA	liquid	NA	NA	
Acrolein, acrylic acid, acetaldehyde	propylene	propylene recovery absorber off-gas	feed	r	air	71^{6}	NA	gas	NA	NA	
	propane		by-product	r	air	3.5^{6}	NA	gas	NA	NA	
	carbon monoxide		by-product	r	air	73.5^{6}	NA	gas	NA	NA	
Acrylic acid, acrylic ester	acetaldehyde	acrylic acid quench-absorber off-gas (oxidation sect.)	by-product	r	air	0.1^{1}	NA	gas	NA	NA	1A
	acetic acid		by-product	r	air	1.4^{1}	NA	gas	NA	NA	
	acetone		by-product	r	air	1.3^{1}	NA	gas	NA	NA	
	acrolein		by-product	r	air	4.5^{1}	NA	gas	NA	NA	
	acrylic acid		product	r	air	18.0^{1}	NA	gas	NA	NA	
	ethyl acrylate		by-product	r	air	1.2^{1}	NA	gas	NA	NA	
	propane		feed	r	air	75.3^{1}	NA	gas	NA	NA	
	water		by-product	r	air	88.6^{1}	NA	gas	NA	NA	
	carbon dioxide		by-product	r	air	269.5^{1}	NA	gas	NA	NA	

TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES (continued)

Product	Pollutant	Location	Source	Release +	Medium	Uncontrolled Emissions kg/kkg product	Rate kg/hr	Form	Controlled Emissions Control Technology	Quantity kg/kkg product	Stream Design.
	carbon monoxide	acrylic acid	by-product	r	air	118.5[1]	NA	gas	NA	NA	
	nitrogen	quench absorber	feed	r	air	4466.6[1]	NA	gas	NA	NA	
	oxygen	off-gas	feed	r	air	128.8[1]	NA	gas	NA	NA	
	propylene		feed	r	air	17.5[1]	NA	gas	NA	NA	
	total VOC		combined	r	air	119.3[1]	817[1]	gas	thermal oxidizer	1.2[1]	
	total VOC	acrylic acid atmospheric equipment	combined	r	air	0.146[1]	< 1[1]	gas	thermal oxidizer	0.002[1]	1B, 1C
	hydrocarbon solvent	extract distillation	feed	r	air	NA	21.64[1]	gas	NA	NA	1D
	acrylic acid	vent from vacumm systems	product	r	air	NA	0.02[1]	gas	NA	NA	
	carbon dioxide		by-product	r	air	NA	0.754[1]	gas	NA	NA	
	oxygen		feed	r	air	NA	0.710[1]	gas	NA	NA	
	nitrogen		feed	r	air	NA	40.24[1]	gas	NA	NA	
	hydrocarbon solvent	foreruns	feed	r	air	NA	4.055[1]	gas	NA	NA	1E
	acrylic acid	distillation	product	r	air	NA	0.01[1]	gas	NA	NA	
	oxygen	vent	feed	r	air	NA	0.370[1]	gas	NA	NA	
	nitrogen	vent	feed	r	air	NA	37.55[1]	gas	NA	NA	
	water	vent	by-product	r	air	NA	0.059[1]	gas	NA	NA	
	total VOC	acrylic acid vacuum equipment	combined	r	air	3.78[1]	25.9[1]	gas	thermal oxidizer	0.04	1D, 1E, 1F, 1G
	hydrocarbon solvent	acrylic acid	feed	r	air	NA	0.193[1]	gas	NA	NA	1F, 1G
	carbon dioxide	distillation	by-product	r	air	NA	0.036[1]	gas	NA	NA	
	oxygen	vent	feed	r	air	NA	0.795[1]	gas	NA	NA	
	water	vent	by-product	r	air	NA	0.157[1]	gas	NA	NA	
	nitrogen	vent	feed	r	air	NA	21.85[1]	gas	NA	NA	
	total VOC	fugitive from pumps	by-product	r	air	NA	1.68[1]	gas	thermal oxidizer	50% collected	1I
	total VOC	fugitive from relief	by-product	r	air	NA	4.16[1]	gas	thermal oxidizer	and 99+%	
	total VOC	fugitive from process valves	by-product	r	air	NA	4.92[1]	gas	thermal oxidizer	reduction	
	total VOC	storage from working	feed, product	r	air	NA	0.431[1]	gas	thermal oxidizer	99+% reduction	
	total VOC	storage from farm	feed, product	r	air	NA	0.539[1]	gas	covered floating roof tanks	85% reduction	

TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES (continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product	Stream Design.
	total VOC	handling from drums	product	r	air	NA	0.0006[1]	gas	thermal oxidizer	99+% reduct.	
	total VOC	handling from tanks	product	r	air	NA	0.0033[1]	gas	thermal oxidizer	99+% reduct.	
	total VOC	handling from barge	product	r	air	NA	0.0017[1]	gas	thermal oxidizer	99+% reduct.	
	total VOC	secondary from quench-adsorber wastewater	combined	r	air	NA	0.208 [1]	NA	NA	NA	
	total VOC	secondary from residues	combined	r	air	NA	0.005 [1]	NA	NA	NA	
Adipic acid cyclohexane	hydrocarbon	raw material storage	feed	r	air	1.1 [3]	NA	gas	NA	NA	
	hydrocarbon	scrubber vent in cyclohexane oxidation section		r	air	20[3]	NA	gas	boiler	negligible [3]	
									thermal incinerator	negligible [3]	
									flaring	2[3]	
									carbon absorber	1[3]	
	carbon monoxide	scrubber vent in cyclohexane oxidation section	by-product	r	air	58 [3]	NA	gas	scrubber + boiler	negligible [3]	
									boiler	0.5 [3]	
									thermal incinerator	negligible [3]	
									flaring	6[3]	
									carbon absorber	58[3]	
	nitrogen oxides	NO_x absorber of nitric oxide	by-product	r	air	27	NA	gas	scrubber + boiler	negligible [3]	
									water scrubber	8[3]	
									thermal reduction	0.5 [3]	
									flaring or combustion	8	
	particulate	adipic acid refining	by-product	r	air	NA	NA	solid	baghouse	< 0.1 [3]	
	nitrogen oxide		by-product	r	air	0.3 [3]	NA	gas	NA	NA	
	hydrocarbon		by-product	r	air	0.3 [3]	NA	gas	NA	NA	
	particulate	adipic acid drying, loading, and storage	product	r	air	NA	NA	solid	baghouse	0.4[3]	
Adipic acid cyclohexyl alcohol	VOC	absorber 2	NA	r	air	0.201 [7]	3.44 [7]	gas	NA	NA	A
	NO_x	absorber 2	by-product	r	air	47.4 [7]	811[7]	gas	NA	NA	A
	adipic acid particulate	adipic acid dryer	product	r	air	0.794 [7]	13.6 [7]	solid			
	adipic acid particulates	adipic acid cooler	product	r	air	78.3[7]	1340.0 [7]	solid	NA	NA	C
	VOC	storage and handling	NA	r	air	0.050 [7]	0.86 [7]	gas	NA	NA	D

TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES (continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product	Stream Design.
	adipic acid particulate	storage and handling	product	r	air	73.0[7]	1250.0[7]	solid	NA	NA	D
	VOC	fugitive	NA	r	air	0.083[7]	1.42[7]	gas	NA	NA	E
	NA	secondary	NA	r	air	negligible[7]	NA	gas	NA	NA	F
Cyclohexanone/ cyclohexyl alcohol	total VOC	high-pressure	combined	r	air	16.9[8]	193[8]	gas	thermal oxidizer	0.169[8]	A
	CO	scrubber vent	by-product	r	air	42.6[8]	486[8]	gas	thermal oxidizer	0.426[8]	A
	total VOC	low-pressure	combined	r	air	2.64[8]	30.1[8]	gas	thermal oxidizer	0.0264[8]	B
	CO	scrubber vent	by-product	r	air	9.72[8]	111[8]	gas	thermal oxidizer	0.0972[8]	B
	organic sodium salt	stripper wastewater	by-product	r	water	200[2]	NA	solid	NA	NA	
	sodium hydroxide	stripper wastewater	feed	r	water	10[2]	NA	solid	NA	NA	
	total VOC	storage and handling	feed, product	r	air	0.841[8]	9.6[8]	gas	internal floating roof on cyclohexane tank	0.155[8]	C
	total VOC	fugitive	combined	r	air	1.72[8]	19.6[8]	gas	detection & repair of major leaks	0.604[8]	D
	total VOC	secondary	combined	r	air	0.0911[8]	1.04[8]	gas	none	-	E
Ethylene oxide	1,2 dichloroethane	process effluent	CO_2 inhibitor	r	water	NA[13]	NA	liquid	NA	NA	
	ethylene	purge reactor system-purge absorber	feed	r	air	47.5[9]	NA	gas	NA	NA	
	ethylene oxide		product	r	air	0.55[9]	NA	gas	NA	NA	
	ethylene	ethylene oxide recovery tail gas scrubber	feed	r	air	0.35[9]	NA	gas	NA	NA	
	ethylene oxide		product	r	air	0.25[9]	NA	gas	NA	NA	
Ethylene oxide/ glycol	ethylene oxide, glycol, polyglycols, etc. (organics)	water effluent	product, by-product	r	air	3.0[9]	NA	liquid	NA	NA	
Formaldehyde methanol with metallic silver catalyst	carbon monoxide	adsorption and purification section - off gases from absorber	by-product	r	air	31.75[3]	NA	gas	NA	NA	
	hydrogen		by-product	r	air	7.6[3]	NA	gas	NA	NA	
	methane		feed	r	air	1.25[3]	NA	gas	NA	NA	
	methanol		feed	r	air	trace[3]	NA	gas	NA	NA	
	formaldehyde		product	r	air	trace[3]	NA	gas	NA	NA	
	dimethyl ether-COD	scrubber waters	by-product	r	water	2.1[3]	NA	liquid	NA	NA	
Glycerin	C_3 hydrocarbons and CO	carbon dioxide stripping tower vent	feed	r	air	61[10]	NA	gas	flare	0.12[10]	A
	acrolein 5% methane 95%	aqueous acrolein receiver vent	product of oxidation step	r	air	3[10]	NA	gas	flare	0.06[10]	A

TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES (continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product	Stream Design.
	acrolein 5% methane 95%	distillation system vent	product of oxidation step	r r	air	7.5[10]	NA	gas	flare	0.15[10]	A
Isophthalic acid	Isophthalic acid,	purification section	product	r	water	NA	NA	liquid	NA	NA	
	terephthalic acid,		by-product	r	water	NA	NA	liquid	NA	NA	
	acetic acid		by-product	r	water	NA	NA	liquid	NA	NA	
Maleic anhydride benzene	oxygen	product recov. absorber	feed	r	air	4,863.0[3]	12,603[11]	gas	NA	NA	A
	nitrogen		feed	r	air	21,406.0[3]	55,470[11]	gas	NA	NA	A
	carbon dioxide		by-product	r	air	972.0[3]	2,517[11]	gas	NA	NA	A
	carbon monoxide		by-product	r	air	680.0[3]	1,761[11]	gas	NA	NA	A
	water		by-product	r	air	1,167.0[3]	3,025[11]	gas	NA	NA	A
	maleic acid		by-product	r	air	2.8[3]	7[11]	gas	NA	NA	A
	formaldehyde		by-product	r	air	14.4[3]	37[11]	gas	NA	NA	A
	formic acid		by-product	r	air	2.8[3]	7[11]	gas	NA	NA	A
	benzene		feed	r	air	67.0[1,3]	173	gas	carbon adsorption incineration	99% reduction	A
	total VOC	product recov. absorber	combined	r	air	86.0[11]	224[11]	gas	carbon adsorption	99% reduction	A
	total VOC	refining vacuum system	combined	r	air	0.1[11]	0.28[11]	gas	vent through absorber	99% reduction	A
									vent through incinerator	99% reduction	B
	benzene	storage and handling	feed	r	air	1.23[11]	3.2[11]	gas	floating-roof tanks	85% reduction	B
	total VOC	storage and handling	combined	r	air	1.27[11]	3.3[11]	gas	NA	NA	C
	benzene	fugitive	feed	r	air	1.13[11]	2.93[11]	gas	detection and correction of major leaks	0.21[11]	C
	total VOC	fugitive	combined	r	air	1.24[11]	3.23[11]	gas		0.34[11]	J
	total VOC	secondary	combined	r	air	0.11[11]	0.3[11]		none	-	

TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES (continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product	Stream Design.
Phenol, acetone cumene	VOC: 0.92% cumene 0.23% other VOC 98.85% spent air ((O_2,N_2,CO_2)	cumene oxidation- Allied technology	combined	r	air	20.630[1,2]	471.00[1,2]	gas	carbon adsorption	0.523[1]	A
	VOC: 0.12% cumene 0.01% other VOC 99.78% spent air 0.09% H_2O	cumene oxidation- Hercules technology	combined	r	air	2.314[1,2]	52.83[1,2]	gas	carbon adsorption	0.523[1]	
	acetophenone	distillation bottoms	by-product	r	water	1.9[4]	NA	liquid	NA	NA	
	phenol		by-product	r	water	0.75[4]	NA	liquid	NA	NA	
	cumyl phenol		by-product	r	water	0.85[4]	NA	liquid	NA	NA	
	total tars		by-product	r	water	50-100[4]	NA	liquid	NA	NA	
	tars containing polycyclic aromatic hydrocarbons		by-product	r	water	NA	NA	liquid	NA	NA	
Phthalic anhydride naphthalene	particulate: phthalic anhydride maleic anhydride naphthalene	main process stream	combined	r	air	28[3]	NA	solid	thermal incinerator scrubber	6[3] 0.3[3]	
	CO		by-product	r	air	50[3]	NA	gas	thermal incinerator scrubber	10[3] 50[3]	
	particulate: phthalic	pretreatment	product	r	air	2.5[3]	NA	solid	thermal incinerator	0.5[3] < 0.1[3]	
	particulate: phthalic anhydride maleic anhydride naphthalene	distillation	combined	r	air	19[3]	NA	solid	thermal incinerator scrubber	4[3] 0.2[3]	
	HC	distillation vent	by-product	r	air	5[3]	NA	gas	thermal incinerator scrubber	1[3] < 0.1[3]	
	phthalic anchydride	distillation light ends	product	r	water	NA	NA	liquid	NA	NA	
	maleic anhydride	distillation light ends	by-product	r	water	NA	NA	liquid	NA	NA	
	phthalic anhydride	distillation bottoms	product	r	water	NA	NA	liquid	NA	NA	
	1,4-naphthaquinone	distillation bottoms	by-product*	r	water	NA	NA	liquid	NA	NA	

TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES (continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product	Stream Design.
Phthalic anhydride o-xylene	particulate: phthalic anhydride maleic anhydride benzoic acid	main process stream-includes reactor and multiple switch condensor	combined	r	air	69^3	NA	solid	scrubber & thermal incinerator thermal incinerator incinerator with steam generator	3^3 4^3 4^3	
	SO_x	main process stream-includes reactor and multiple switch condensor	by-product	r	air	4.7^3 for fresh catalyst 9.5 to 13^3 for aged	NA	gas	same as above same as above	0% reduction^3 0% reduction^3	
	CO		by-product	r	air	151^3	NA	gas	scrubber & thermal incinerator thermal incinerator incinerator with steam generator	6^3 8^3 8^3	
	particulate: phthalic anhydride	pretreatment	combined	r	air	6.4^3	NA	solid	scrubber & thermal incinerator	0.3^3	
	maleic anhydride	pretreatment							thermal incinerator	0.4^3	
	particulate: phthalic anhydride maleic anhydride benzoic acid	distillation	combined	r	air	45^3	NA	solid	scrubber & thermal incinerator thermal incinerator	2^3 2^3	
	HC	distillation	by-product	r	air	1.2^3	NA	gas	scrubber & thermal incinerator thermal incinerator	$<0.1^3$ $<0.1^3$	
	phthalic anhydride	distillation light ends	product	r	water	20^3	NA	liquid	NA	NA	
	maleic anhydride	distillation light ends	by-product	r	water	NA	NA	liquid	NA	NA	
	phthalic anhydride	distillation bottoms	product	r	water	NA	NA	liquid	NA	NA	
Terephthalic acid	nitrogen oxides	reactor	by-product	r	air	6.5^3	NA	gas	NA	NA	
	some organic vapor-mainly xylene	off-gas scrubber in reaction	feed	r	air	NA	NA	gas	NA	NA	
	acetic acid	section	feed	r	water	NA	NA	liquid	NA	NA	
	acetic acid & catalyst	solvent recovery unit	feeds	r	water	NA	NA	liquid	NA	NA	
	terephthalic acid	centrifuge	product	r	water	NA	NA	liquid	NA	NA	

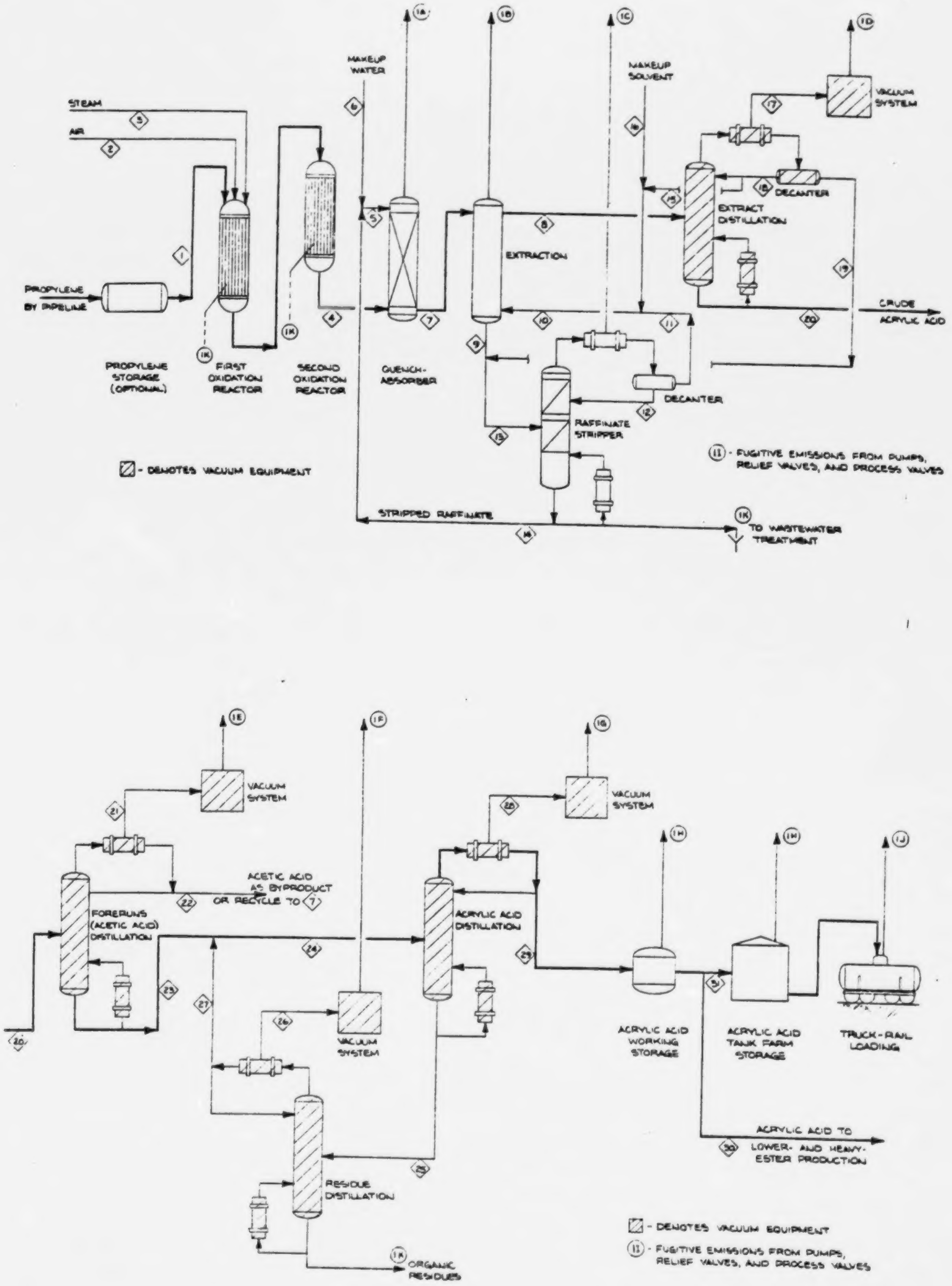
TABLE 18-2. ESTIMATED RELEASES FOUND IN SOME OXIDATION PROCESSES (continued)

						Uncontrolled Emissions			Controlled Emissions		
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product	Stream Design.
Total water flow - 159-932 ℓ/kkg	COD	wastewater streams	NA	r	water	(2.5-227)^{2}	NA	NA	NA	NA	
	BOD		NA	r	water	(1-68)^{2}	NA	NA	NA	NA	
	TOC		NA	r	water	(1-34)^{2}	NA	NA	NA	NA	

Sources: (1)White 1980, Vol. 10. Based on 76,000 kkg/yr capacity.
(2)Hedley 1975. Based on 45,400 kkg/yr capacity.
(3)AP 42 1981.
(4)Background Document 1980. Based on average production of 1000 kkg/yr for 1976.
(5)White 1980, Vol. 10. Based on 200,000 kkg/yr capacity.
(6)Hedley 1975. Based on 9,000 kkg/yr capacity.
(7)White 1980, Vol. 6. Based on 150,000 kkg/yr capacity.
(8)White 1980, Vol. 6. Based on 100,000 kkg/yr capacity.
(9)Hedley 1975. Based on 29,500 kkg/yr capacity.
(10)White 1980, Vol. 10. Production basis not stated.
(11)White 1980, Vol. 6. Based on 22,700 kkg/yr capacity.
(12)White 1980, Vol. 7. Based on 200,000 kkg/yr capacity.
(13)Wise and Fahrenthold 1981. Concentrations reported are greater than 0.5 ppm. Feedstock is ethylene.

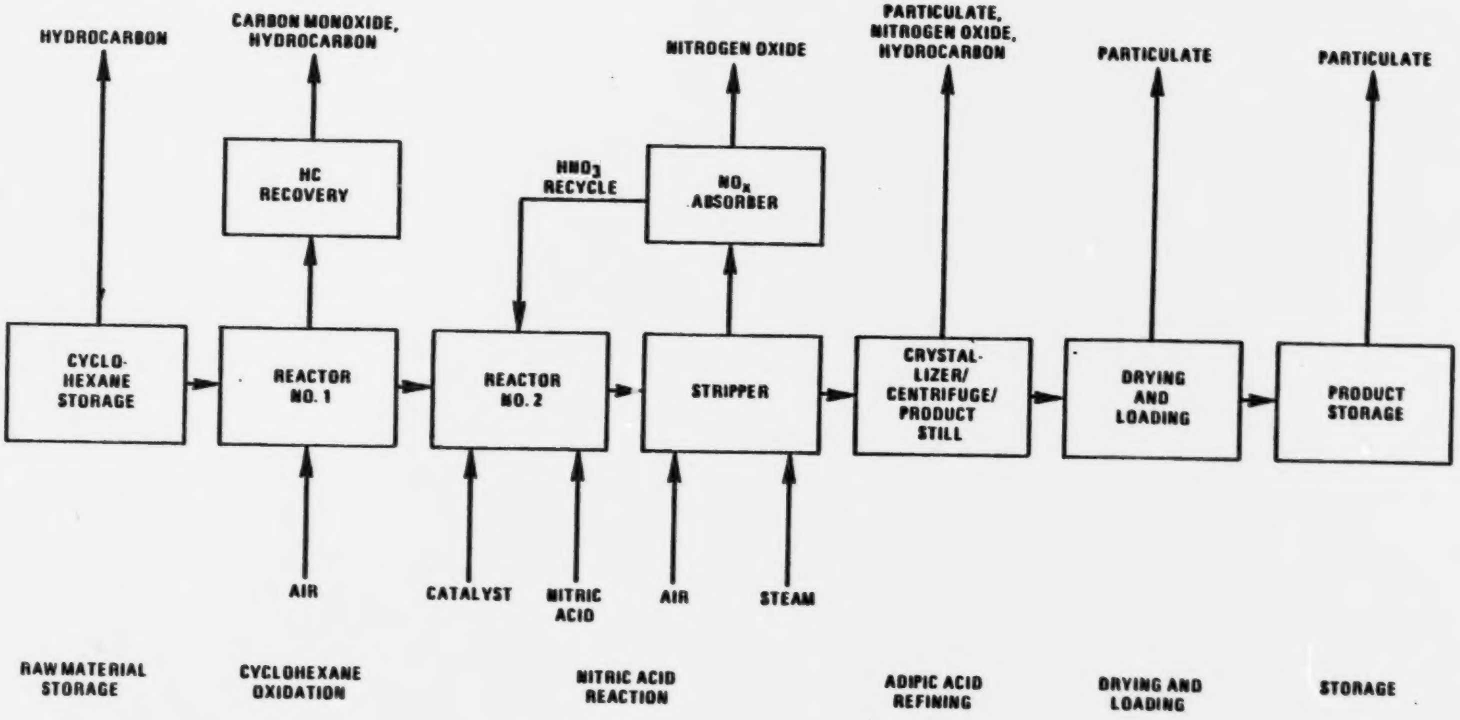
Some oxidation processes have more than one product.

FIGURE 18-3. MANUFACTURE OF ACRYLIC ACID FROM PROPYLENE



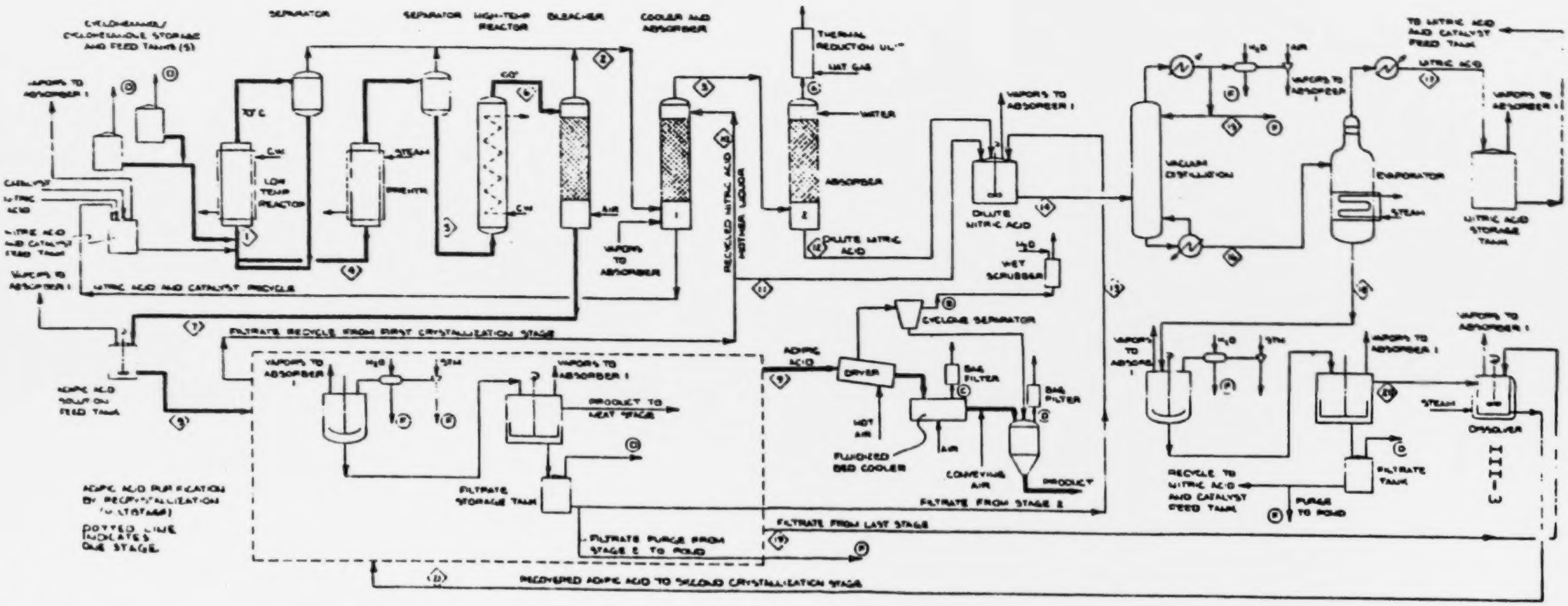
Source: White 1980.

FIGURE 18-4. GENERAL FLOW DIAGRAM OF ADIPIC ACID MANUFACTURE FROM CYCLOHEXANE



Source: USEPA 1981.

FIGURE 18-5. PROCESS FLOW DIAGRAM FOR MANUFACTURE OF ADIPIC ACID FROM CYCLOHEXYL ALCOHOL



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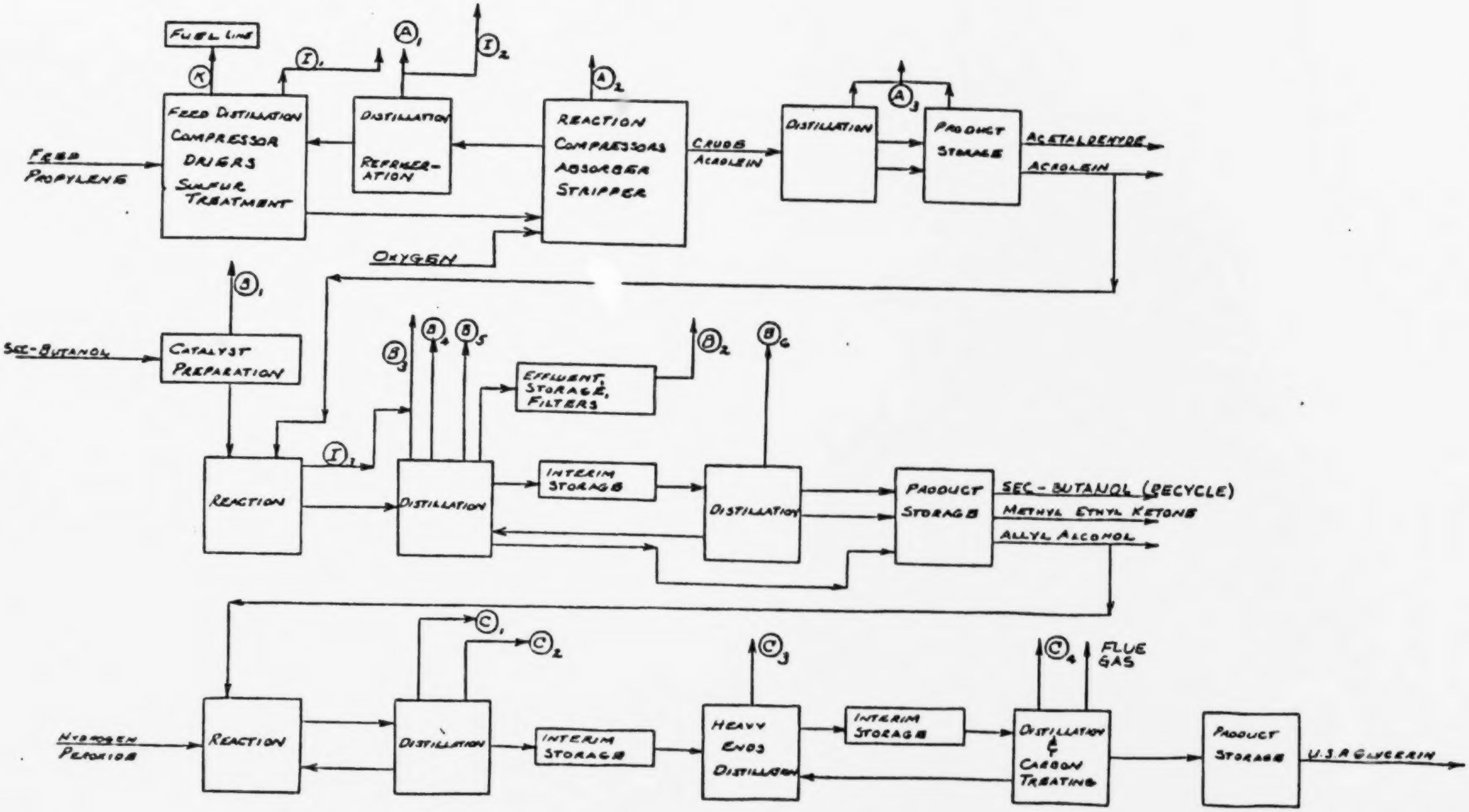
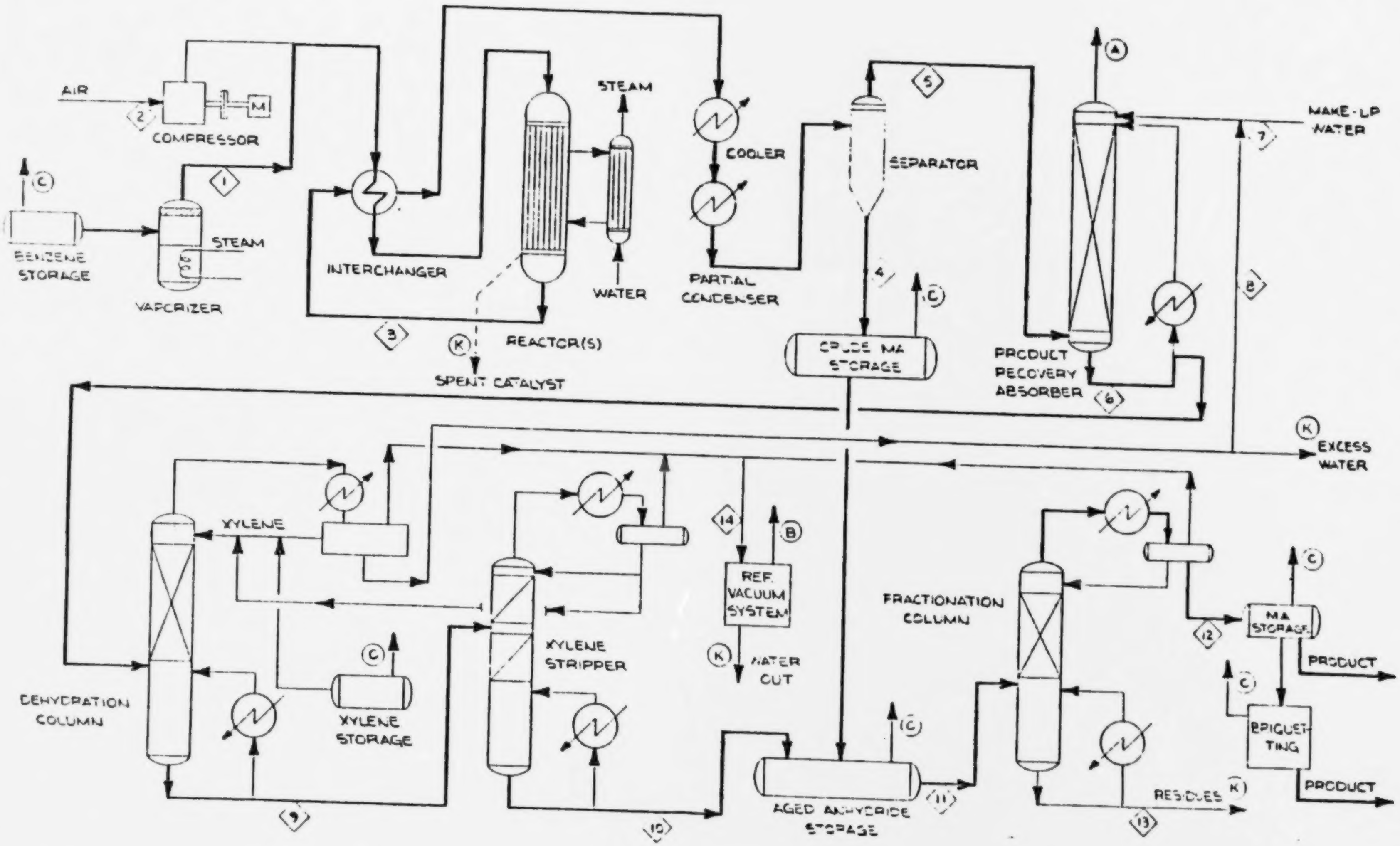
Source: White 1980.

FIGURE 18-6. BLOCK FLOWSHEET OF OXIDATION PROCESS FOR UNCONTROLLED MODEL PLANT PRODUCING SYNTHETIC GLYCERIN



Source: White 1980.

FIGURE 18-7. PROCESS FLOW DIAGRAM FOR MODEL PLANT OF UNCONTROLLED MALEIC ANHYDRIDE MANUFACTURE BY BENZENE OXIDATION



Source: White 1980.

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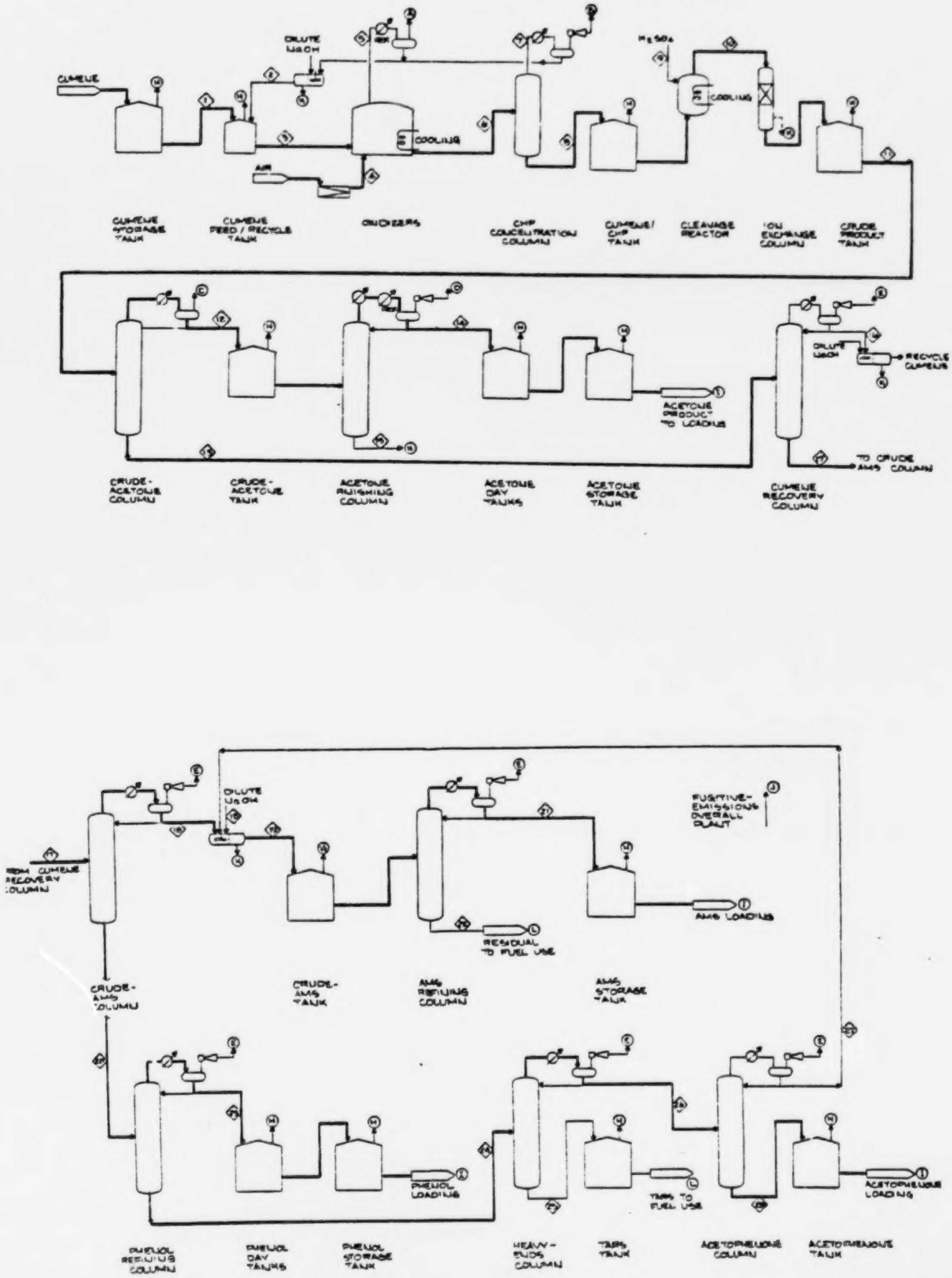
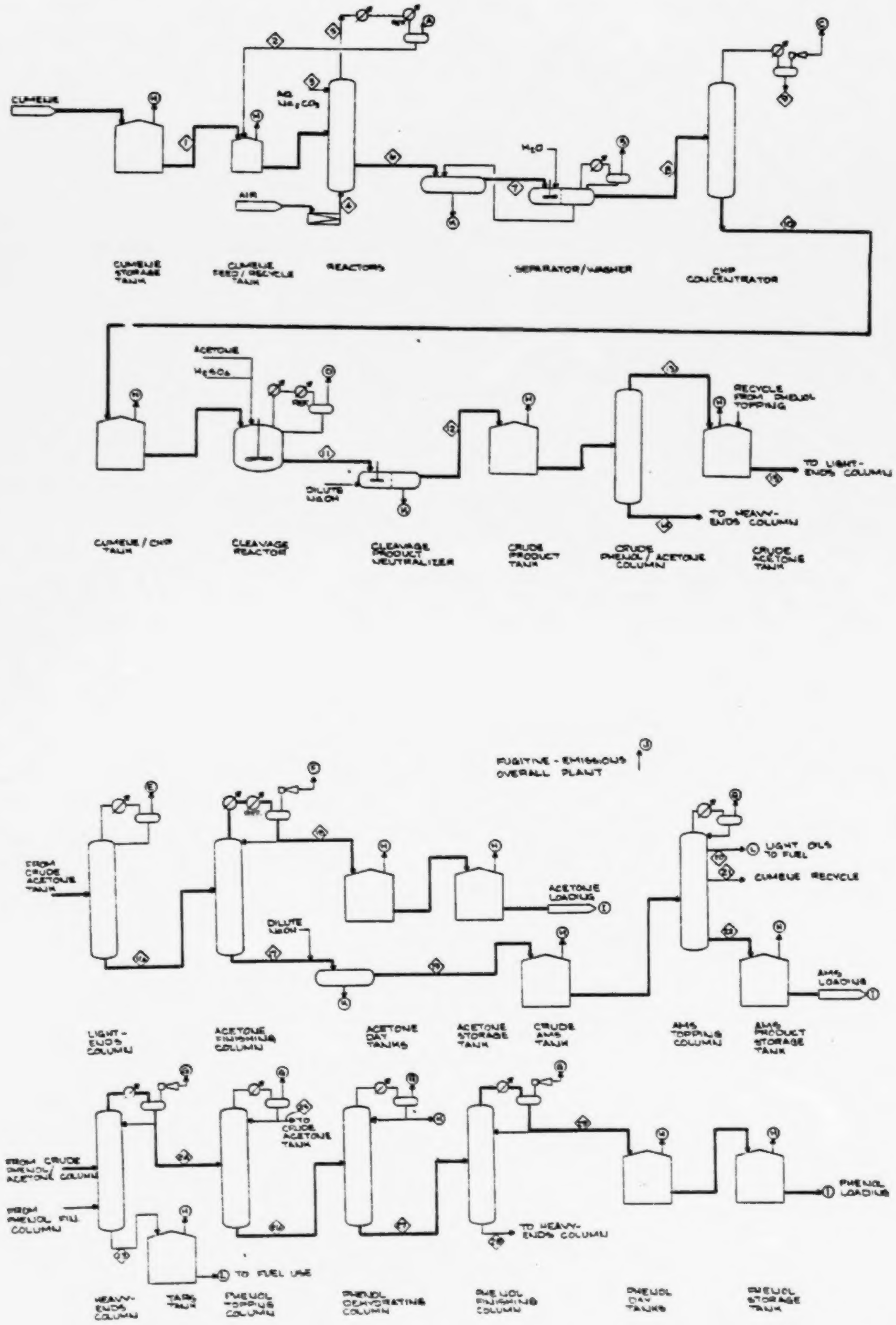
FIGURE 18-8. FLOW DIAGRAM FOR PHENOL/ACETONE FROM CUMENE USING ALLIED TECHNOLOGY



Source: White 1980.

FIGURE 18-9. FLOW DIAGRAM FOR PHENOL/ACETONE FROM CUMENE USING HERCULES TECHNOLOGY



Source: White 1980.

REFERENCES

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals, 3rd Ed. New York: John Wiley and Sons, Inc.

Gruber, G. I., TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. U.S.Environmental Protection Agency. Office of Solid Waste. Washington, D. C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitg, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Company, Inc.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Kirk-Othmer. 1979. Encyclopedia of Chemical Technology, 3rd Ed. Volumes 2 and 4. New York: John Wiley and Sons, Inc.

Shreve, R. N. 1967. Chemical Process Industries, 3rd Ed. New York, New York: McGraw Hill Book Company.

U.S. EPA. Office of Solid Waste, November 14, 1980. Background Document. Resource Conservation and Recovery Act, Subtitle C - Identification and Listing of Hazardous Waste. Listing of Hazardous Wastes (Finalization of May 19, 1980 Hazardous Waste List).

U.S. EPA. 1981. Supplement 12 for Compilation of Air Pollutant Emission Factor. Research Triangle Park, North Carolina: U.S. EPA, Office of Air and Water Management and Office of Air Quality Planning and Standards.

USITC. 1979. United States Production and Sales. Synthetic Organic Chemcials. U.S. Department of Commerce.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 10. U.S.Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028e.

Wise, H., and Fahrenthold, P. November 1981. Predicting Priority Pollutants from Petrochemical Processes. Environ. Sci. and Techn., 15, (11), pp. 1292-1304.

REFERENCES CONSULTED BUT NOT USED

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Kent, James A. 1974. Riegel's Handbook of Industrial Chemistry. New York: Van Nostrand Reinhold Company.

SECTION 19 - OXYHALOGENATION

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SECTION 19

OXYHALOGENATION

19.0 INTRODUCTION

In the oxyhalogenation process, a halogen acid is catalytically oxidized to the halogen with air or oxygen. Commercial applications of the process use oxychlorination in which chlorination is accomplished by catalytically oxidizing hydrogen chloride to chlorine with air or oxygen (Herrick 1979). This process has also been termed oxyhydrochlorination.

The oxychlorination process uses a reactor with either a fluidized bed with internal cooling coils or a tubular fixed-bed with the catalyst inside the tubes and the coolant in the shell (Considine 1974; White 1980). Table 19-1 presents the chemicals produced, production volumes, other processes required, and the feedstock required for this process. Figure 19-1, the production of trichloroethylene, is a flow diagram for a typical oxyhalogenation process.

The Environmental Protection Agency has designated vinyl chloride, ethylene dichloride, perchloroethylene, trichloroethylene and phenol as priority pollutants. Each pollutant has been shown to damage the liver, kidney, and other organs through various exposure routes (USEPA 1980).

19.1 GENERAL CHEMISTRY

Oxyhydrochlorination involves the chlorination of a hydrocarbon with hydrogen chloride and oxygen or compressed air. A typical reaction can be represented by a general chemical equation, for example:

$$\text{hydrocarbon} + \text{oxygen (air)} + \text{hydrogen chloride} \longrightarrow \underset{\text{hydrocarbon}}{\text{chlorinated}} + \text{water} + \text{(by-products)}$$

TABLE 19-1. OXYHALOGENATION PRODUCTS[1] AND THEIR MANUFACTURE IN 1979[2]

Product	Amount kkg	Feedstock	Other Required Processes
Ethylene dichloride	5,350,000	Ethylene	none
Perchloroethylene	350,640	Any C_2	Halogenation
Trichloroethylene	144,892	Chlorocarbon mixture	Catalytic cracking
Phenol	36,552[3]	Benzene, HCl	Hydrolysis
Vinyl chloride monomer	NA	Ethane Chlorine	Dehydrohalogenation Halogenation
Vinyl chloride monomer	1,823,440[4]	Ethylene Chlorine	Dehydrohalogenation Halogenation
Vinyl chloride monomer	NA	Naptha Chlorine	Dehydrohalogenation Halogenation

Source:

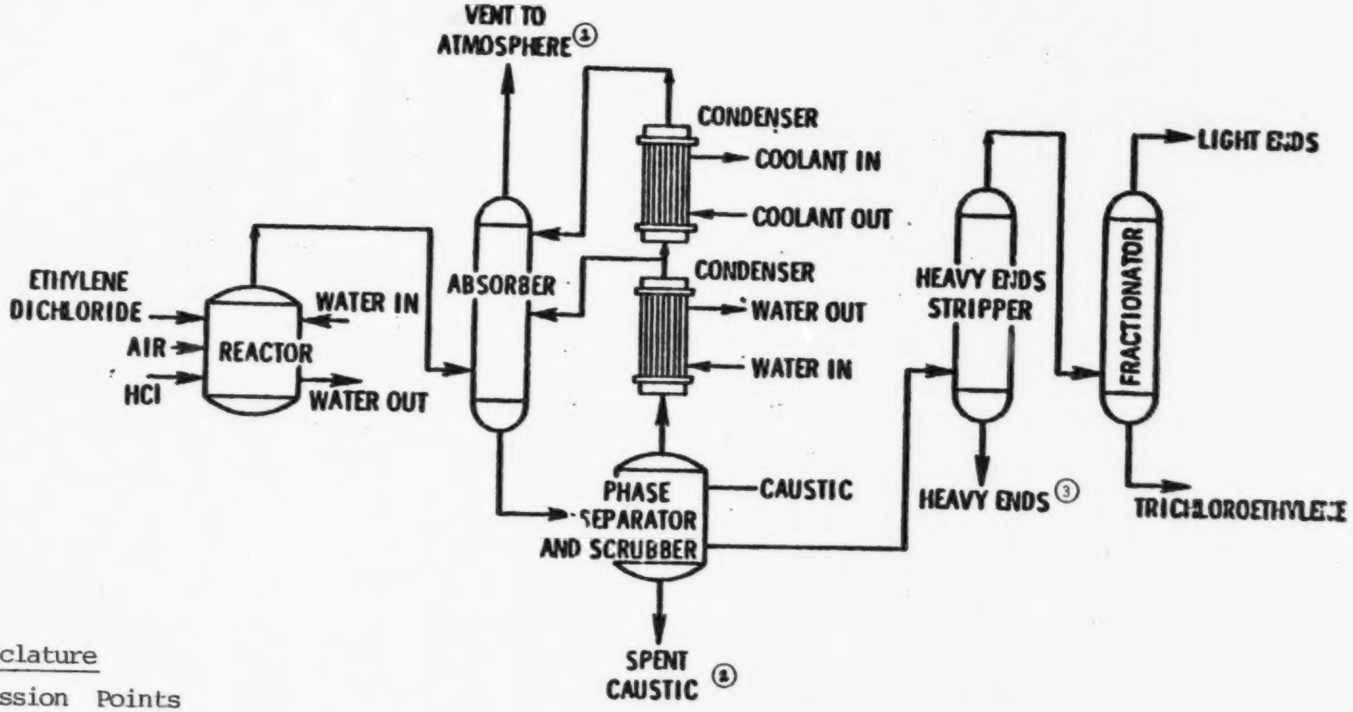
[1] Herrick 1979.

[2] USITC 1979. Total Production From All Processes.

[3] Includes all phenol produced with the exception of phenol from cumene, production, coke ovens, and gas-retort ovens.

[4] SRI 1981. Production levels are assumed to be 80% of plant nameplate capacity.

FIGURE 19-1. MANUFACTURE OF TRICHLOROETHYLENE BY OXYCHLORINATION



Nomenclature

O Emission Points

SOURCE: Khan and Hughes 1979.

A typical case of oxyhalogenation is the oxyhydrochlorination of ethylene dichloride to produce trichloroethylene:

$$O_2 + HCl + ClCH_2CH_2Cl \longrightarrow C_2HCl_3 + 2H_2O$$

Copper chloride is used as a catalyst in a vapor phase reaction at 300°C to 400°C with the reaction pressure of 100 psig. The reaction is usually exothermic and is dependent upon various factors including the hydrocarbon and the catalyst used, reaction temperature and pressure, and the ratio of hydrogen chloride to the hydrocarbon (Khan and Hughes 1979).

19.2 DESCRIPTION OF DISCHARGES

Oxyhalogenation manufacturing process emissions usually consist of hydrocarbons. These may be feedstock, impurities in the feedstock, products, and by-products. Table 19-2 (adapted from Khan and Hughes 1979) summarizes unit operations and identifies emission points in some typical oxyhalogenation manufacturing processes.

Emissions from two typical oxyhalogenation manufacturing processes may be classified under the headings of fugitive, process, secondary, and storage and handling:

Fugitive emissions - occur from pressure relief valves, flanges, pump seals, valve steams and compressors. When process pressures are higher than cooling water pressure, VOC can leak into the cooling water and escape as a fugitive emission from the cooling tower.

Process emissions - from absorber vents which release inert gases from the oxygen, chlorine, hydrogen chloride, and other feeds; drying column releases or non-condensable gases; and neutralizer vents.

Secondary emissions - from wastewater containing VOC in the waste treatment system and from the combustion of tars in the incinerator.

TABLE 19-2. UNIT OPERATIONS INVOLVED IN THE OXYHALOGENATION MANUFACTURE OF CHLORINATED HYDROCARBONS WITH EMISSION SOURCES IDENTIFIED

		Unit Operation								
Product	Manufacturing process	Absorption	Drying	Fluid flow	Heat transfer	Material handling	Mixing	Separation	Storage	Waste disposal
Ethylene dichloride	Oxyhydrochlorination of ethylene	A	-	D	D	D	-	A W S	A	W S
Trichloroethylene	Oxyhydrochlorination of ethylene dichloride	A	-	D	D	D	D	W S	A	W S

Source: Khan and Hughes 1979.

[a] A = Atmospheric emission; W = Wastewater discharge; S = Solid waste; D = Unit operation performed but no process emissions anticipated; - = Unit operation not performed.

Storage and handling emissions - sources are feedstock storage, recycle storage, product storage, loading of product into containers for shipment.

19.3 PRODUCTION PROCESS: THE MANUFACTURE OF ETHYLENE DICHLORIDE FROM ETHYLENE AND HYDROGEN CHLORIDE

Ethylene dichloride (EDC) is produced by direct chlorination or by oxychlorination of ethylene. Most production facilities in the United States use a balanced combination of both processes (White 1980; Versar 1979). The production of EDC by oxychlorination of ethylene can be represented by the following chemical reaction:

$$\underset{\text{(ethylene)}}{2CH_2{=}CH_2} + \underset{\text{(oxygen)}}{O_2} + \underset{\text{(hydrogen chloride)}}{4HCl} \longrightarrow \underset{\text{(ethylene dichloride)}}{2ClCH_2CH_2Cl} + \underset{\text{(water)}}{2H_2O}$$

Air and hydrogen chloride react with ethylene in a fixed or fluid-bed, vapor phase, catalytic reaction to produce EDC. The catalyst, usually cupric chloride, is highly reactive and selective and produces high conversion and EDC purity in a one-stage reaction (Considine 1974). Reaction temperature varies between 180 and 280°C and pressure between 50 and 100 psig). The basic steps for the manufacture of EDC by this process are:

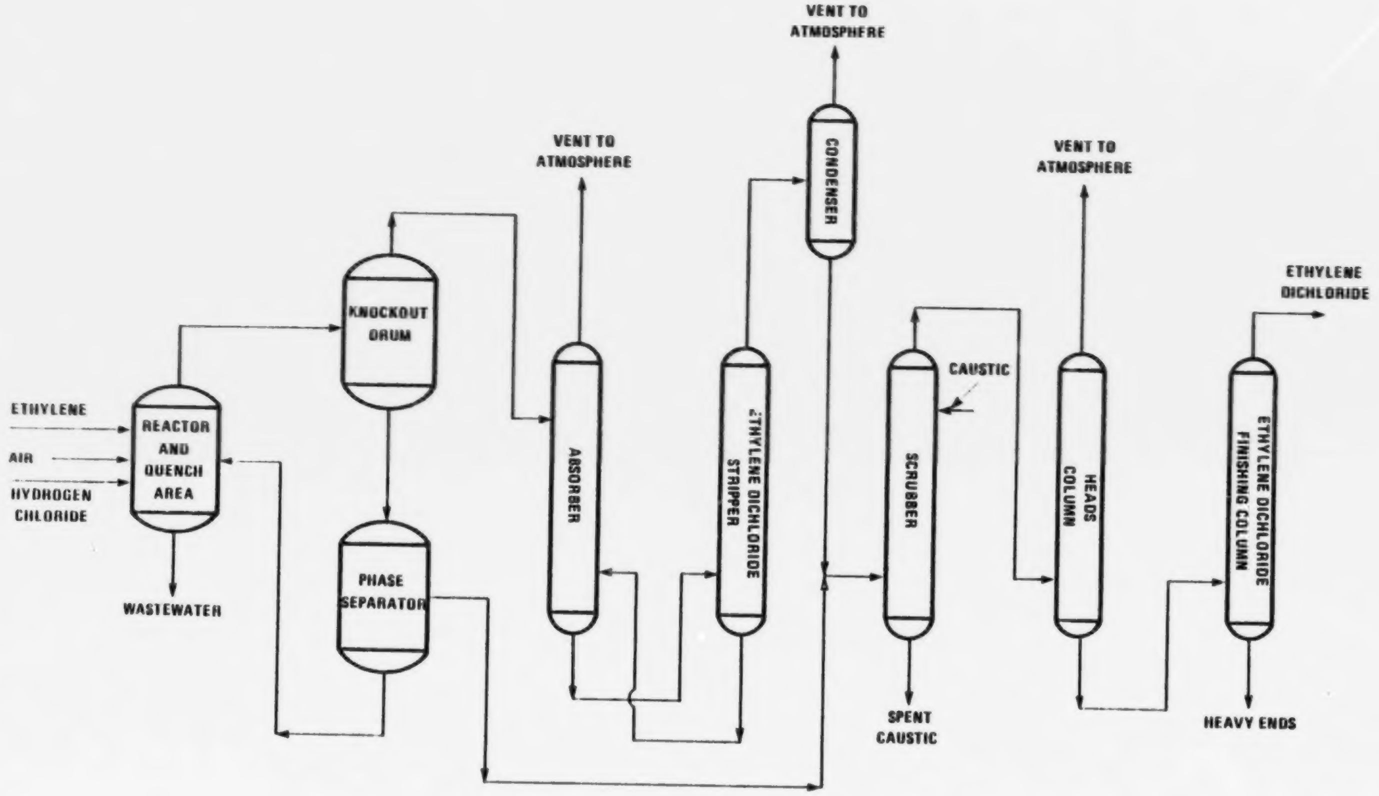
- oxychlorination
- separation
- absorption
- purification

The best available information on the production of EDC by this process is found in White 1980, Khan 1979, Versar 1979, and Considine 1974. Figure 19-2 is a flow diagram for the production of EDC by oxychlorination.

19.3.1 Oxychlorination

Stoichiometric proportions of ethylene, anhydrous hydrogen chloride (HCl), and air are fed by pipeline to the oxychlorination reactor. The

FIGURE 19-2 ETHYLENE DICHLORIDE MANUFACTURE BY THE OXYCHLORINATION PROCESS
SOURCE: KHAN AND HUGHES 1979.



reaction is highly exothermic; therefore, it requires adequate heat removal for proper temperature control. The effluent from the oxychlorination reaction is cooled by either direct water quench or indirect heat exchange. Unreacted HCl in the effluent gas is absorbed in water in the quench column.

19.3.1.1 Emissions from Oxychlorination and Quenching

Water quenching cools the gases very rapidly by direct contact with water in a quench tower. Condensable hydrocarbons, i.e., unreacted HCl, are removed at this step. The resulting waste stream is treated in a wastewater stripper, which results in potential secondary emissions.

19.3.2 Separation

The reactor effluent is sent to a knockout drum where crude EDC and water are separated from the non-condensable gases. The EDC and water phases are separated in a decanter (phase separator) and the water phase is passed offsite for treatment. The crude EDC phase is combined with crude EDC from the direct chlorination process (if the balanced process is used) for purification.

19.3.2.1 Emissions from Separation

Emissions will occur from leaks developed in the equipment used for product separation.

19.3.3 Absorption and Stripping

The non-condensed material, consisting mainly of nitrogen, from the knockout drum, is passed to an absorber where EDC is recovered from nitrogen and other inert gases. The absorbed stream is sent to a stripper where crude EDC is passed overhead and the stripped absorbent is recycled to the absorber.

19.3.3.1 Emissions from Absorption and Stripping

The largest amount of emissions from the oxychlorination process is emitted from the absorber. The off-gases from the oxychlorination reaction are vented to the atmosphere from the absorber. The emission stream contains nitrogen from the air fed to the reactor, ethane from the ethylene feed, carbon dioxide, and carbon monoxide formed from side reactions. Some EDC and other chlorinated hydrocarbons not recovered by the absorber are also emitted.

19.3.4 Product Purification

Crude EDC from the stripper and the phase separator is neutralized with aqueous caustic soda in a scrubber to remove any residual hydrogen chloride and carbon dioxide. Effluent from the caustic scrubber is distilled in a heads column for removal of any remaining water and chlorinated hydrocarbon impurities. These impurities are vented overhead and sent to waste disposal. Light ends are removed for liquid waste storage, sales, or waste disposal. Bottoms from the heads column consisting mainly of EDC are sent to the final products finishing column. Pure EDC is obtained as an overhead stream and sent to storage; the bottoms consisting of heavy ends (tars) are sent to sales or disposal.

19.3.4.1 Emissions from Purification

Process emissions to the atmosphere will occur from vent gases from the condenser and the heads column. The chlorinated hydrocarbons by-products (overheads from the heads column and bottoms from the finishing column) can be incinerated if they are not converted to marketable solvents. The incineration of these liquid waste streams is a potential secondary emission source where VOC are emitted with the flue gases.

SUMMARY OF DISCHARGES

Emissions data are provided for:

1) Ethylene dichloride (Table 19-3, Figure 19-2).

2) Trichloroethylene (Table 19-4, Figure 19-2).

3) Perchloroethylene and Trichloroethylene (Table 19-5, Figure 19-3).

4) Vinyl Chloride Monomer (Table 19-6, Figure 19-4).

Releases are characterized as either routine (r) or accidental (a), controlled or uncontrolled. Emissions data were not found for phenol production by oxyhalogenation.

TABLE 19.3 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE DICHLORIDE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Ethylene dichloride	absorber vent	product	r	air	.46[7]-7.[1]	NA	gas	NA	NA
Ethylene		feedstock	r	air	.332[7]-5.3[1]	NA	gas	NA	NA
Ethane		by-product	r	air	0.3[1]	NA	gas	NA	NA
Other VOC		by-product	r	air	29[1]	NA	gas	NA	NA
Nitrogen		feedstock	r	air	770[1]	NA	gas	NA	NA
Oxygen		feedstock	r	air	46[1]	NA	gas	NA	NA
Carbon dioxide		by-product	r	air	24[1]	NA	gas	NA	NA
Carbon monoxide		by-product	r	air	7.3[1]	NA	gas	NA	NA
Total VOC		feed/by-product	r	air	7.17[3]	327[3]	gas	Thermal Oxidizer	.00717[3]
Ethylene dichloride		product	r	air	3.24[3]	148[3]	gas		.000324[3]
Ethylene dichloride	overhead stream from knockout drum	product	r	air	1[2]	NA	gas	NA	NA
Ethylene		feedstock	r	air	18[2]	NA	gas	NA	NA
Ethane		by-product	r	air	0.3[2]	NA	gas	NA	NA
Other VOC		feed/by-product	r	air	1[2]	NA	gas	NA	NA
Nitrogen		feedstock	r	air	10[2]	NA	gas	NA	NA
Oxygen		feedstock	r	air	2[2]	NA	gas	NA	NA
Carbon dioxide		by-product	r	air	30[2]	NA	gas	NA	NA
Carbon monoxide		by-product	r	air	3[2]	NA	gas	NA	NA
Total VOC		feed/by-product	r	air	9.39[4]	429[4]	gas	Thermal Oxidizer	.00939[4]
Ethylene dichloride		product	r	air	.462[4]	21.1[4]	gas		.000462[4]
Total VOC	column vents	feed/by-product	r	air	13[5]	594[5]	gas	Thermal Oxidizer	.0130[5]
Ethylene dichloride		product	r	air	3[5]	137[5]	gas		.003[5]
Ethylene	entrainment separator	feedstock	r	air	2.6[6]	NA	gas	NA	NA
Carbon monoxide		by-product	r	air	1.2[6]	NA	gas	NA	NA
Ethylene dichloride		product	r	air	8.15[6]	NA	gas	NA	NA
Vinyl chloride		by-product	r	air	8.5[6]	NA	gas	NA	NA
Dichloroethylene		by-product	r	air	.45[6]	NA	gas	NA	NA
Vinylidene chloride		by-product	r	air	.05[6]	NA	gas	NA	NA
Methane and ethane		feedstock	r	air	.45[6]	NA	gas	NA	NA
Hydrogen chloride	surge and decanter vessels	feedstock	r	land	.35[6]	NA	gas	NA	NA

TABLE 19.3 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE DICHLORIDE MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Chlorine/HCl	absorber	feedstock	r	air	.0019[7]	NA	gas	NA	NA
Carbon tetrachloride		by-product	r	air	<.003[7]	NA	gas	NA	NA
Methane		feedstock	r	air	.988[7]	NA	gas	NA	NA
Chloroform		by-product	r	air	<.005[7]	NA	gas	NA	NA
Methylene chloride		by-product	r	air	<.003[7]	NA	gas	NA	NA
Vinyl chloride		by-product	r	air	.01[7]	NA	gas	NA	NA
Trichloroethane		by-product	r	air	<.005[7]	NA	gas	NA	NA
Ethylene	separation train (distillation columns)	feedstock	r	air	.00001[7]	NA	gas	NA	NA
Cl/HCl		feedstock	r	air	.005[7]	NA	gas	NA	NA
Ethylene dichloride		product	r	air	.085[7]	NA	gas	NA	NA
Methylene dichloride		by-product	r	air	.0015[7]	NA	gas	NA	NA
Vinyl chloride		by-product	r	air	.012[7]	NA	gas	NA	NA
Chloroform		by-product	r	air	.042[7]	NA	gas	NA	NA
Carbon tetrachloride		by-product	r	air	.094[7]	NA	gas	NA	NA
Ethyl chloride		by-product	r	air	.047[7]	NA	gas	NA	NA
1,1,-Dichloroethane		by-product	r	air	.004[7]	NA	gas	NA	NA
Methane		feedstock	r	air	.000004[7]	NA	gas	NA	NA
Vinylidene chloride		by-product	r	air	.00009[7]	NA	gas	NA	NA
Dichloroethylene		by-product	r	air	.00008[7]	NA	gas	NA	NA
Hydrocarbons	oxychlorination with incineration of vent gases	feedstock/ by-products	r	air	25[8]-70[8]	600-1670[8]	gas	99%[8]	.25-.7[8]

Sources:

[1] White 1980. Based on oxychlorination process using air. Plant capacity is 185,000 kkg per year.
[2] Ibid 1980. Oxychlorination using oxygen. Plant capacity is 185,000 kkg per year.
[3] Ibid 1980. Emissions from the balanced process using air. Plant capacity is 400,000 kkg per year.
[4] Ibid 1980. Emissions from the balanced process using oxygen. Plant capacity is 400,000 kkg per year.
[5] Ibid 1980. Emissions from column vents from balanced process; use of either air or oxygen was not specified.
[6] Hedley et al. 1975. Plant capacity is 73,483 kkg per year.
[7] Khan and Hughes 1979.
[8] TRC, 1976.

+Emissions are routine (r)

TABLE 19.4 CHARACTERIZATION OF EMISSIONS FROM THE TRICHLOROETHYLENE PRODUCTION PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Ethylene dichloride	absorber	feed	r	air	13	NA	gas	NA	NA
Trichloroethylene		product	r	air	8.5	NA	gas	NA	NA
Carbon tetrachloride		by-product	r	air	13	NA	gas	NA	NA

Source: Khan and Hughes 1979.

+ Emissions are routine (r)
4

TABLE 19-5. CHARACTERIZATION OF EMISSIONS FROM TRICHLOROETHYLENE AND PERCHLOROETHYLENE*

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
VOC	reactor	feed/by-product	r	air	21.3	NA	gas	Thermal	70^1
Hydrogen chloride	vent	feed	r	air	0.5	NA	gas	oxidizer and	NA
Carbon dioxide		feed	r	air	65.5	NA	gas	H_2O scrubbers	NA
Nitrogen		feed	r	air	7.1	NA	gas		
Vinyl chloride	drying column vent	by-product	r	air	.52	NA	gas	NA	NA
Vinylidene chloride		by-product	r	air	.40	NA	gas	NA	NA
Perchloroethylene/ Trichloroethylene		product	r	air	.0075	NA	gas	NA	NA
VOC		feed/by-product	r	air	.62	NA	gas	NA	NA
Trans - dichloroethylene		by-product	r	air	.65	NA	gas	NA	NA
Nitrogen		feed	r	air	.30	NA	gas	NA	NA
Trans - dichloroethylene	distillation vent	by-product	r	air	.225	NA	gas	NA	NA
Cis - dichloroethylene		by-product	r	air	.063	NA	gas	NA	NA
Vinylidene chloride		by-product	r	air	.098	NA	gas	NA	NA
Perchloroethylene		product	r	air	.075	NA	gas	NA	NA
Trichloroethylene		product	r	air	.075	NA	gas	NA	NA
Other VOC		feed/by-product	r	air	.012	NA	gas	NA	NA
Nitrogen		feed	r	air	.029	NA	gas	NA	NA

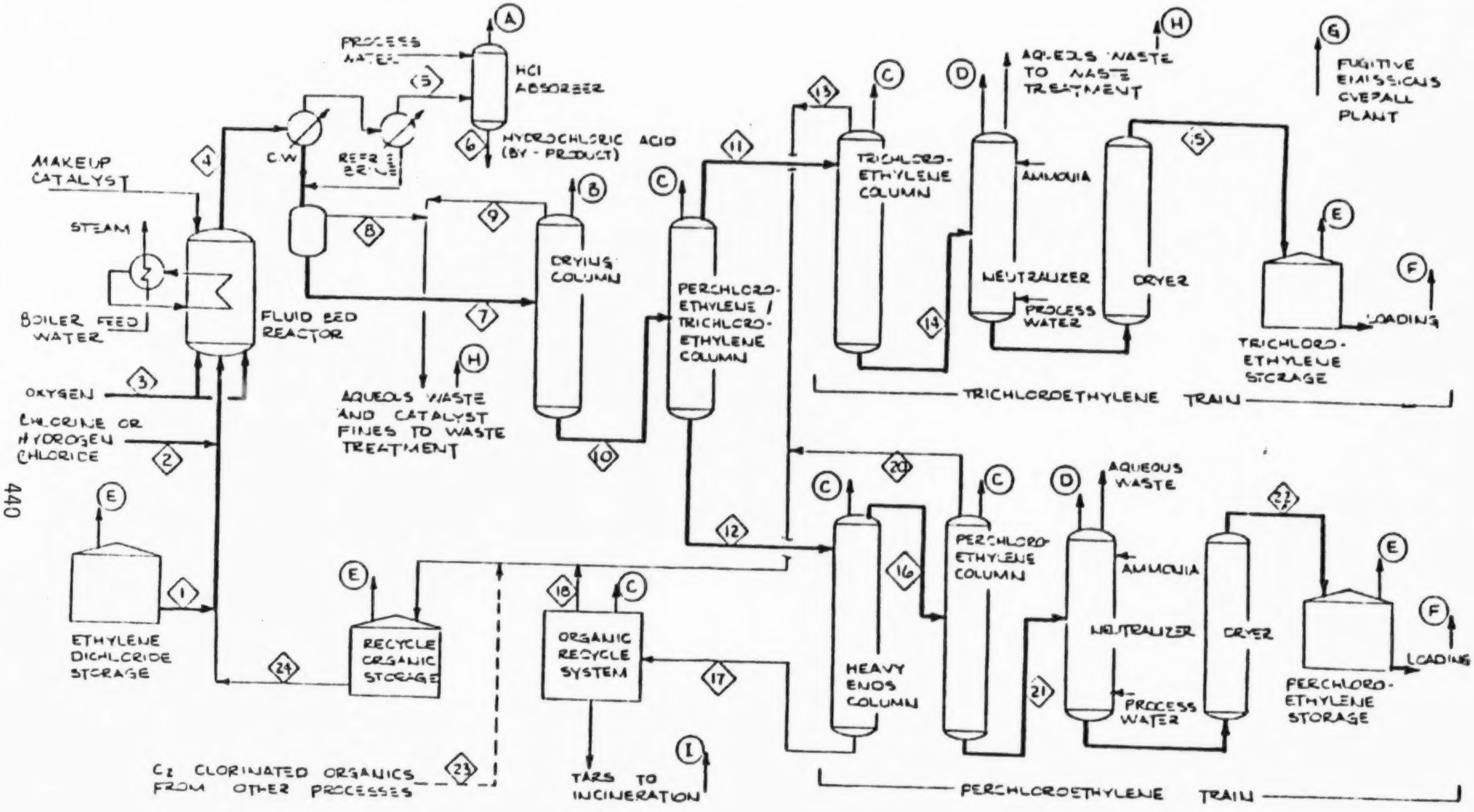
Source: White 1980. Vol. 8. Report 4.

[1] Estimate of current industry emissions from the oxychlorination process for perchloroethylene and trichloroethylene production.

*Perchloroethylene and trichloroethylene are produced as co-products by the oxychlorination process. The name plate capacity for this plant is 180,000 kkg per year.

+Releases are routine (r).

FIGURE 19-3. FLOW DIAGRAM FOR PERCHLOROETHYLENE AND TRICHLOROETHYLENE BY OXYCHLORINATION



Source: White 1980, Vol. 8.

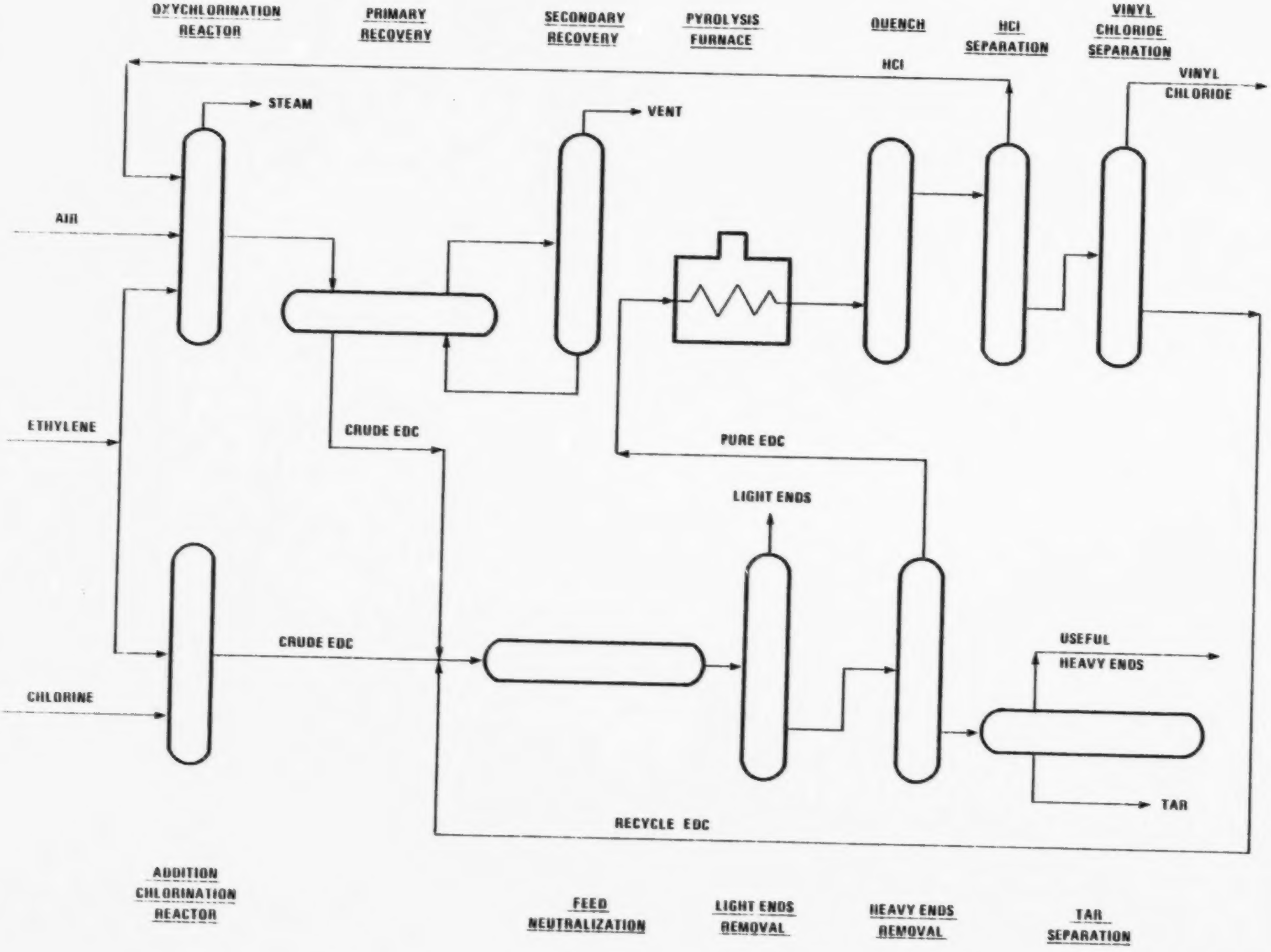
Reproduced from best available copy.

TABLE 19-6. CHARACTERIZATION OF EMISSIONS FROM VINYL CHLORIDE MONOMER PRODUCTION

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
Vinyl chloride	NA	product	air	4.1-5.3	NA	gas	NA	NA	NA

Source:USEPA 1975. Emissions are from a combination of direct chlorination and oxychlorination processes in which the HCl produced in cracking is recycled to the oxychlorination process. Emission numbers are based on estimated atmospheric emission loss of 0.45 percent of vinyl chloride produced in monomer plants operating at full capacity.

FIGURE 19–4 FLOW DIAGRAM FOR PRODUCTION OF VINYL CHLORIDE FROM ETHYLENE AND CHLORINE. SOURCE: HYDROCARBON PROCESSING, 1973.



REFERENCES

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Hedley, W.H., S.M. Mehta, C.M. Moscowitz et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Technomic Publishing Company, Inc. Westport, Connecticut.

Herrick, E.C., J.A. King, and R.P. Ouellette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Khan, Z.S., and T.W. Hughes. Monsanto Research Corporation. 1979. Source Assessment: Chlorinated Hydrocarbons Manufacture. Industrial Environmental Research Laboratory. Research Triangle Park, North Carolina: U.S. Environmental Protection Agency. EPA-600/2-79-019G.

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

TRC. The Research Corporation. 1976. Controlled and Uncontrolled Emission Rates and Applicable Limitations for Eighty Processes. Prepared for USEPA/OAQPS, Research Triangle Park, North Carolina.

White, R.E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 8. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028c.

USITC. 1979. United States Production and Sales. Synthetic Organic Chemicals. U.S. Department of Commerce.

Versar Inc. 1979. Production and Use of 1,2-Dichloroethane. For: Office of Water Planning and Standards. Washington, D.C.: U.S. Environmental Protection Agency.

USEPA. 1980. Background Document. Resource Conservation and Recovery Act. Subtitle C - Identification and Listing of Hazardous Waste. Washington, D.C.: Office of Solid Waste.

USEPA. 1975. Scientific and Technical Assessment Report on Vinyl Chloride and Polyvinyl Chloride. Research Triangle Park, North Carolina: Office of Research and Development, Environmental Research Center.

REFERENCES EVALUATED BUT NOT USED

Faith, W.L., D.B. Keyes and R.L. Clark. 1965. Industrial Chemicals. 3rd Ed. New York, New York: John E. Wiley and Sons, Inc.

Gruber, G.I. TRW Systems Group.. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides and Explosives Industries. For: U.S. Environmental Protection Agency. Office of Solid Waste. Washington, D.C. EPA/530/SW-118C.

Morrison, R.T., and R.N. Boyd. 1978. Organic Chemistry, 3rd Ed. Boston, Massachusetts: Allyn and Bacon, Inc.

Shreve, N. 1967. Chemical Processes Industries, 3rd Ed. New York, New York: McGraw Hill Book Company.

Versar Inc. 1980. Environmental Assessment of Priority Pollutants. Task 15: Preparation of Standard Pollutant Tabs. EPA Contract No. 68-01-3852. For: Office of Water Planning and Standards, Washington, D.C.

USEPA. 1974. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemical Manufacturing Industry. Point Source Category. Washington, D.C.

SECTION 20 - PHOSGENATION

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SECTION 20

PHOSGENATION

20.0 INTRODUCTION

Phosgenation is the process in which phosgene reacts with an amine to form an isocyanate or in which phosgene reacts with an alcohol to form a carbonate (Herrick 1979). Chemicals that are produced by the phosgenation process are:

- Toluene diisocyanate (TDI)
- Diphenylmethane - 4,4' diisocyanate (MDI)
- Polycarbonate resins

Table 20.1 presents pertinent processes and feedstocks require to manufacture each chemical.

Most commercial TDI plants produce the intermediates dinitrotoluene (DNT), toluene diamine (TDA), and phosgene (White 1980). The production of TDA is a catalytic process; however, the phosgenation of TDA to produce TDI is a thermal process. Figure 20.1 is a flow diagram for a typical phosgenation process.

20.1 GENERAL CHEMISTRY

Diisocyanate

Toluene dissocyanate (TDI) and diphenylmethane 4-4' diisocyanate (MDI) are particularly suitable for the production of polyurethane foams. Both chemicals serve as intermediates in the manufacture of rigid foams (Herrick et al. 1979a; Pistor et al. 1977). The reaction for 2,4 TDI from 2,4-toluene diamine and phosgene is:

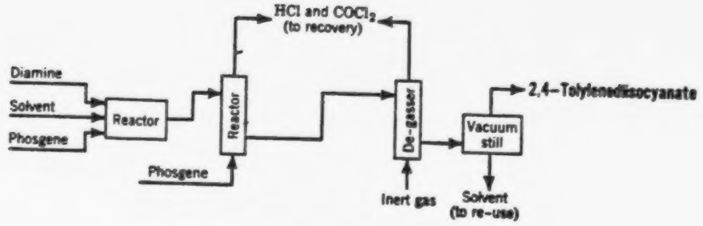
TABLE 20-1. PHOSGENATION PRODUCTS AND THEIR MANUFACTURE IN 1980†

Product	Amount kkg	Feedstock	Other Required Processes
Diphenylmethane-4,4'diisocyanate [methylene bis(4-phenylisocyanate)] (MDI)	260,816	Aniline Formaldehyde Phosgene	None
Polycarbonate resins	151,953	Bisphenol A Phosgene	Dehydrogenation Polymerization
Toluene diisocyanate (TDI)I 80/20, 2,4,-2,6-TDI	324,318	Phosgene Toluene	Hydrogenation

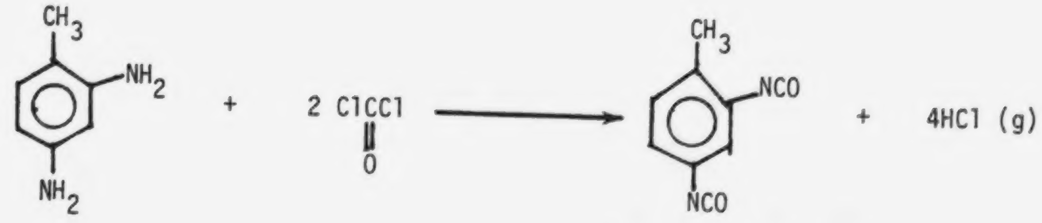
Sources: Herrick et al. 1979a
SRI, 1981

†Levels of manufacture are based on plant nameplate capacities with unspecified production processes.

FIGURE 20-1. A TYPICAL PHOSGENATION PROCESS



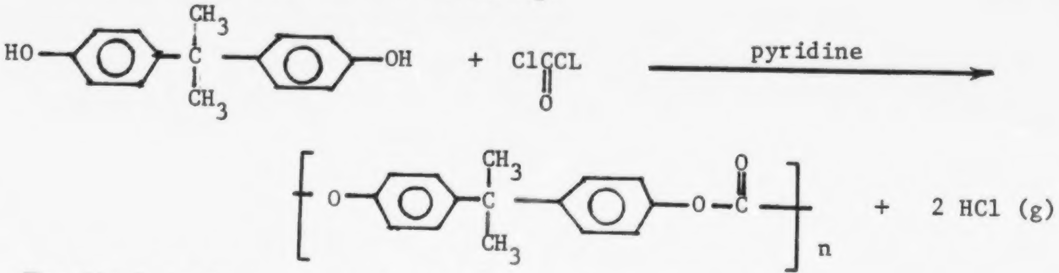
Source: Faith et al. 1965



Phosgene reacts with TDA to yield TDI and hydrogen chloride.

Polycarbonate Resins

Polycarbonate resins have numerous applications in the thermoplastics industry (Modern Plastics Encyclopedia 1980-1981). The best available information on polycarbonate production is found in Considine (1974). Polycarbonate resins are manufactured by the phosgenation of a dehydroxy aromatic (bisphenol A). Phosgene, bisphenol A, pyridine (acid acceptor), and a phosgenation solvent are reacted in a polymerization reactor. This reaction is depicted in the following:



The final products are polycarbonates plus hydrogen chloride.

20.2 DESCRIPTION OF DISCHARGES

Wastestreams will contain fugitive emissions from valves, gas compressors, wastewater treatment systems, and cooling water systems. Emissions to the atmosphere can be expected from distillation unit vents, pump seals and flanges, and catalyst incineration. Solid waste will include polymeric residue as a result of product purification.

White (1980) reports that phosgene is ~ 99% of the estimated uncontrolled VOC emissions associated with the solvent recovery and TDI product distillations.

20.3 PROCESS DESCRIPTION: MANUFACTURE OF DIISOCYANATE

TDI and MDI are produced by very similar processes with similar reactions and emissions. Both products result from dissolving a primary amine in a phosgenation solvent and reacting it with phosgene and separating the evolved hydrogen. Because the demand for TDI is greater, this product has been picked for the process description. The three basic steps for phosgenation are 1) phosgenation, 2) separation, and 3) purification. Figure 20.2 is a generalized flow diagram for TDI production.

20.3.1 Phosgenation

TDI is produced by dissolving a primary diamine (TDA) in a phosgenation solvent and reacting it with phosgene. Phosgenation solvents are usually aromatic hydrocarbons or halogenated aromatic hydrocarbons such as chlorobenzenes (Faith et al. 1965).

The phosgenation apparatus consists of 2 or 3 agitated reactors in series depending upon the production method of the individual producer. Phosgene is mixed in reactor 1 (capacity ~1000 parts volume) with the phosgenation solvent/diamine solution at a temperature of ~5-10°C (Pistor et al. 1977). In reaction II (capacity ~1500 parts by volume), and reaction III (capacity ~2500 parts by volume) the reaction temperature is increased to ~20-80°C and 110-130°C, respectively (Pistor et al. 1977). Hydrogen chloride and unreacted phosgene (gas) are processed off from reactors II and III (Beck 1958). These gases are then passed through a washing column where the unreacted phosgene is removed from recycling into reactor I. The hydrogen chloride vapors are absorbed by water and sold to steel mills to be used for metal pickling (Wood 1981). The phosgenation products will contain the diisocyanate corresponding to the primary diamine, phosgene solvent, unreacted phosgene, hydrogen chloride, and heavy phosgenation by-products.

20.3.1.1 Emissions from Phosgenation

Since phosgenation by-products are gaseous, emissions will occur at valves, flanges, seals, and leaks in the equipment. These emissions will include hydrogen chloride.

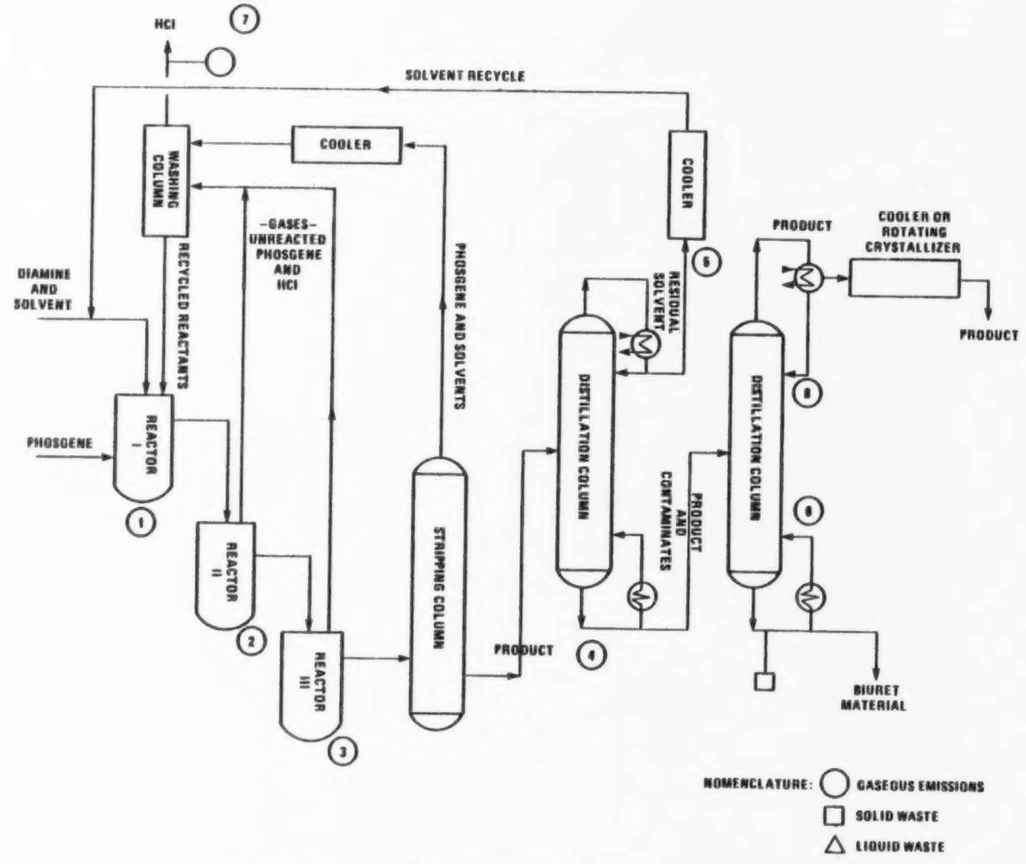


FIGURE 20.2 FLOW DIAGRAM FOR DIISOCYANATE PRODUCTION

SOURCE: ADAPTED FROM PISTOR, 1977. AND NERSASIAN, 1975.

20.3.2 Separation

After phosgenation, the solvent and unreacted phosgene are separated from the diisocyanates by degassing and stripping. The stripping columns separate the dissolved gases from the liquid product. Both reactants are cooled, washed, and recycled into reactor I.

20.3.2.1 Emissions from Separation

Emissions known to occur from strippers are due to leaks at valves, flanges, and seals in the equipment. These emissions would include phosgene and phosgenation solvents as gases. The cooling water in the cooling column will become contaminated as the result of leaks in the equipment. A wastewater stream containing dissolved hydrogen chloride, phosgene, and phosgenation solvent will be generated in the washing column. Disposal of the water is not known; however, a stripper is probably employed and the dissolved gases are recycled. Depending on the efficiency of the stripper, the cleaned water from the stripper may contain a very small amount of contaminants. Gaseous emissions may occur from the washing column.

20.3.3 Purification

The phosgenation products are fractionally distilled to remove the residual solvent which then follows the same cooling and washing cycle as the previously removed solvent. The diisocyanate product is further distilled at the approximate temperature range of 180-220°C to remove the phosgenation by-products. The heavy phosgenation by-products are polymeric materials containing biuret molecules bearing free isocyanate groups and carbodiimide impurities (Nersasian, 1975). Nersasian also has reported that the undistilled phosgenation product will contain approximately 10-30% by-products by weight.

The diisocyanate biuret material is drawn off the bottom of the distillation column and is stockpiled in some instances as a potential energy source or can be incinerated.

The diisocyanate product is passed into a cooling column if the desired product is TDI liquid. MDI can be sold as solid flakes or as a liquid solution. If solid flakes are desired, the MDI will be processed through a crystallizer. If a liquid product is desired, the MDI will be cooled in a cooling column and solvent will be added.

20.3.3.1 Emissions from Purification

Emissions will result from valves, flanges, seals, and leaks from the distillation columns. Intermittent emissions will occur at the relief vents on the distillation columns. These emissions will be organic emissions and not inorganic emissions such as phosgene or hydrogen chloride.

The cooling water in the cooling towers will become contaminated with TDI or MDI because of leaks in the tower. Particulate emissions will occur from the crystallizer because it is flaking the MDI solid. If a solvent is added to the MDI, solvent emissions may occur from the cooling tower.

20.3.4 Polycarbonate Resins

Polycarbonate resins are produced when phosgene, bisphenol A, pyridine and a phosgenation solvent are reacted in a polymerization reactor. The reaction mixture consists of the polycarbonate polymer, pyridine hydrochloride, and unreacted pyridine in solvent. This mixture goes to a wash tank where water and HCl are added, the acid reacting with the residual pyridine to make a by-product, pyridine hydrochloride. The polymer solution is separated from the pyridine hydrochloride solution by decantation. An antisolvent is added to the polymer solution to precipitate the polycarbonate in a slurry form. The slurry is filtered, and the solid polycarbonate is dried to a powder. The solvent and the antisolvent that are separated in the decanting and the drying steps proceed to the solvent recovery operation for recycling preparation. Hedley et al. (1975) have reported that emissions of solvents and raw materials during the reaction, and of resins and solvents during storage and handling, are probable major sources of air contamination.

Figure 20-3 is the flow diagram for a typical polycarbonate production process (Sittig 1962).

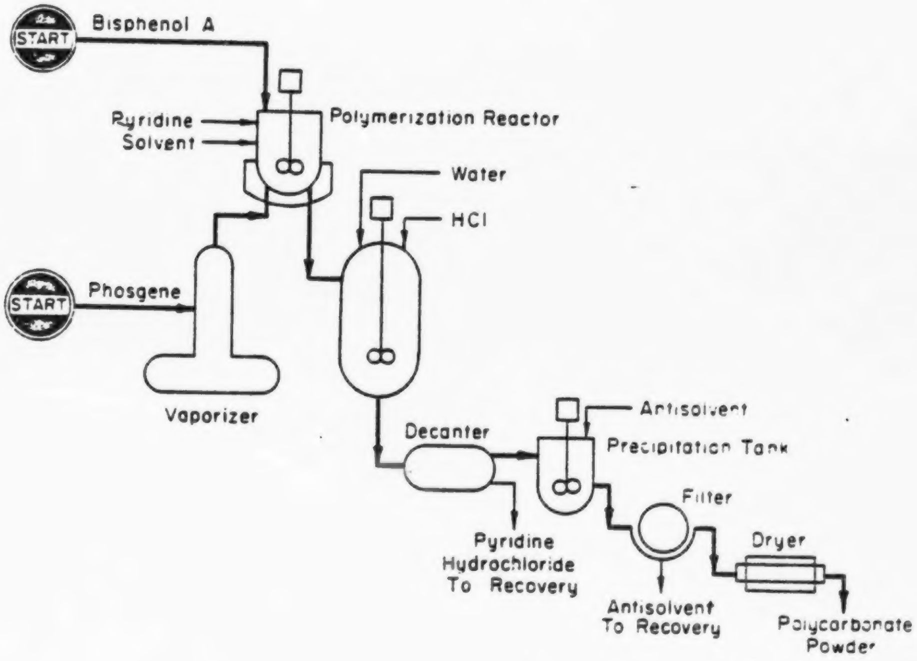
20.4 SUMMARY OF EMISSIONS DATA

Emissions data are provided for the following manufacturing processes:

- TDI (Table 20-2)
- MDI (Table 20-3)
- polycarbonate resin (Table 20-4)

The location of emissions sources for Table 20-2 is found by consulting Figure 20-2. Releases are characterized as either routine (r) or accidental (a), controlled or uncontrolled.

FIGURE 20-3 FLOW DIAGRAM FOR POLYCARBONATE PRODUCTION



Source: Sittig, 1962

TABLE 20-2. CHARACTERIZATION OF EMISSIONS FROM THE TDI MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
organic amines	TDA reactor (1x2) catalyst separative unit	feedstock	r	air	.0005[1]	.0026[1]	gas	wet Venturi scrubber for particulate removal	1.0×10^{-4} 1
	distillation vacuum jets		r	air	.0033[1]	.017[1]	gas	water cooled surface condensers for removal of organic amines	1.0×10^{-4} 1
VOC emission containing phosgene and dichlorobenzene	vacuum-jet hot wells solvent recovery (5) TDI purification (3,8,4)	feedstock and solvent	r	air	4.6[1]	23.8[1]	gas	dilute caustic scrubber or hydrolysis column column for phosgene removal	.046[1]
chlorinated hydrocarbons	vacuum-jet hot wells	by-product	r	air	1.1×10^{-5} 1	5.7×10^{-5} 1	gas	water cooled surface condensers	3.3×10^{-7} 1
phosgene CO_2	HCl absorber and acid recovery section (7)	feedstock	r	air	4.6×10^{-7} 1	2.4×10^{-6} 1	gas	packed water scrubber (hydrolysis column for control of trace phosgene)	9.2×10^{-9} 1
HCl	acid absorption section waste scrubber (7)	by-product	r	water	24.9[2]	NA	liquid	NA	NA
polymers and tarry matter	TDI purification (6) column	by-product	r	land	19.1[2]	NA	solid	NA	NA
ferric chloride		by-product	r	land	1.4[2]	NA	solid	NA	NA
Chloroaromatics	process effluent	by-product	r	water	NA[3]	liquid	NA	NA	NA

---

[1] Source: White (1980), Vol. 7. p. IV-3. Based on 45,000 kkg/yr capacity.
[2] Source: Hedley et al. (1975). Based on 13,000 kkg/yr capacity.
[3] Wise and Farenthold, 1981. Concentrations reported were greater than 0.5 ppm. Toluenediamine is the feedstock.
*Indicates that release is routine (r) or accidental (a).

TABLE 20-3. CHARACTERIZATION OF EMISSIONS FROM THE MDI MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Impurities	Isocyanate recovery	MDI purification	r	land	157.2	NA	solid	NA	NA

Source: Hedley et al. (1975). Based on 2,300 kkg/yr capacity.

+Indicates that release is routine (r).

TABLE 20-4. CHARACTERIZATION OF EMISSIONS FROM THE POLYCARBONATE RESIN MANUFACTURING PROCESS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
sodium chloride	pyridine recovery section - azeotrope column waste to sewer	product separation	r	water	760	NA	land	NA	NA

Source: Hedley et al. (1975). Based on 9,100 kkg/yr capacity.

+Indicates that release is routine (r).

REFERENCES

Beck, T. R. 1958. Process for the Manufacture of Organic Isocyanates. Patent Δ2,8222,373.

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals. 3rd ed. New York: John Wiley and Sons, Inc.

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemicals. Westport, Connecticut: Technomic Publishing Co., Inc.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Nersasian, A. 1975. Storage of Stable Crude Isocyanates and Production Thereof. U. S. Patent Δ3,914,269.

Pistor, H. J., H. Hoffman, H. Joschek, and G. Wenner. 1977. Manufacture of 4,4'-Diphenylmethane Diisocyanate and a Mixture of Diisocyanates and Polyisocyanates. U. S. Patent Δ4,014,914.

Sittig, M. 1962. Organic Chemical Processes. The Noyes Press, Inc. Pearl River, New York.

SRI International. 1981. Directory of Chemical Producers - United States. Menlo Park, California.

White, R. E. 1980. IT Enviroscience. Organic Chemical Manufacturing. Vol. 7. For U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Research Triangle Park, NC. EPA-450/3-80-028b.

Wise, Hugh E. Jr. and Paul D. Fahrenthold. November 1981. Predicting Priority Pollutants from Petrochemical Processes, Environmental Science and Technology, 15, (11), pp. 1242-1304.

Wood, Patricia. Versar, August 1981. Personal communication with Don Kimble, Allied Chemical, Moundsville, West Virginia.

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SECTION 21

POLYMERIZATION

21.0 INTRODUCTION

Polymerization is the process where simple molecules, i.e., monomers, are reacted to form polymers. Plastics, rubbers, textiles, lubricants, and coatings are examples of products composed of polymers. Two types of polymerization may occur: condensation polymerization and addition polymerization. Addition polymerization is when the molecules of monomer are added together to form polymer chains. The common reaction is the opening of a carbon-to-carbon double bond to permit growth of polymer chains by attachment to the carbons. Condensation polymerization occurs in two steps: first, two different molecules join together emitting water, methanol, or hydrogen chloride and then the resulting products join to form polymer chains. Examples of each type of polymerization are shown under Section 21.1.

The organic chemicals most frequently made by polymerization and their amounts produced in 1979 are listed in Table 21-1. Note that when polymers are formulated from two or three different reactants, the polymer is made by condensation polymerization.

Most polymerizations are catalytic reactions at high pressure. The catalysts, also called initiators, are usually in a solution or a slurry with a solvent which is a hydrocarbon diluent. Chain transfer agents, antioxidants, and shortstops are added to the reaction to obtain the desired chain length. Plasticizers and stabilizers are added to obtain polymer characteristics such as heat and chemical resistance, flexibility, or rigidity.

Polymerization processes generally follow a process sequence of 1) reactants and solvent purification, 2) reaction and product concentration, 3) blending and solvent removal, and 4) drying and packaging. Reactants and solvent purification include fractionating columns, driers, and caustic and water washes. The purified reactants, solvents, catalysts, and chain-length determinants are then fed to the polymerization reactors. The

TABLE 21-1. ORGANIC CHEMICALS MANUFACTURED BY POLYMERIZATION[1]

Products	Annual Production (kkg 1979)[2]	Reactants	Other Required Processes
Acrylic resins	517,856	acrylonitrile	
Acrylonitrile-butadiene-styrene resins (ABS)	567,665	acrylonitrile butadiene styrene	
Epoxy resin	217,595	bisphenol A epichlorohydrin	
Ethylene-propylene copolymer resins	176,389	ethylene or propylene	
Ethylene-vinyl acetate copolymer resins	-	ethylene vinyl acetate	
Polyamide resins (Nylon 6)	131,091	caprolactum	
Polyamide resins (Nylon 66)		adipic acid hexamethylene diamine	
Polybutadiene[3]	9,281	butadiene	
Polybutadiene-acrylonitrile (NBR)	73,253	acrylonitrile butadiene	
Polybutenes	-	butene-1/butene-2	
Polycarbonate resins	-	bisphenol A phosgene	dehydrohalogenation phosgenation
Polychloroprene (neoprene)	83,163	chloroprene	
Polyester resins (saturated)	267,660	glycols polybasic acids styrene	
Polyester resins[4] (unsaturated)	536,036	glycols styrene unsaturated dibasic acids	
Polyether glycols	830,497	ethylene oxide propylene oxide	
Polyether glycols		ethylene oxide propylene oxide alcohols	

TABLE 21-1. ORGANIC CHEMICALS MANUFACTURED BY POLYMERIZATION[1] (Continued)

Products	Annual Production (kkg 1979)[2]	Reactants	Other Required Processes
Polyethylene (low density)	3,393,853	ethylene	
Polyethylene (high density)	2,234,543	ethylene	
Polyethylene terephthalate	172,847	ethylene glycol terephthalic acid	esterification
Polyethylene terephthalate		dimethylterephthalate ethylene glycol	condensation
Polyisobutylene	-	isobutene butenes	
Polyisocyanate	129,264	organic dichlorides sodium cyanate	pyrolysis
Cis-polyisoprene	-	isoprene	
Polypropylene	1,734,513	propylene	
Polystyrene	1,062,650	styrene	
Polystyrene (high impact-rubber modified)	682,268	polybutadiene styrene	
Polyvinyl acetate	410,135	vinyl acetate	
Polyvinyl alcohol resins	75,591	vinyl alcohol	
Polyvinyl chloride resins	2,817,481[5]	vinyl chloride	
Polyvinyl chloride-acetate copolymer	-	vinyl acetate vinyl chloride	
Polyvinyl chloride-vinylidene chloride copolymer resins	9,908	vinyl chloride vinylidene chloride	
Propylene tetramer	-	propylene	
Styrene-butadiene resin[3] (SBR)	1,641,766	styrene butadiene	
Urea-formaldehyde resin	624,918	biuret formaldehyde urea	

---

[1] Source: Herrick; 1980

[2] Source: USITC, Synthetic Organic Chemicals; 1979

[3] Solution and emulsion polymerization

[4] Annual production includes polyethylene terephthalate, polybutylene terephthalate, and other saturated polyester resins

[5] Value includes polyvinyl chloride copolymers

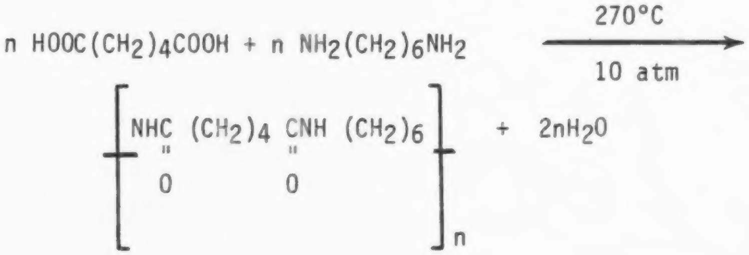
products pass to a concentration step to remove the suspended catalysts. This step may have settlers, centrifuges, degassers, and caustic and water washes. The recovered catalysts are recycled to the reactor. Plasticizers, stabilizers, dyes and pigments, etc., are added to the products in the blending step to obtain the desired product. The solvent and unreacted reactants are removed by distillation and liquid-liquid extraction or strippers, and recycled. Treatment after polymerization varies with proposed use. The resins may be dried, cut, and baled if a solid product is desired. Resins for molding are dried and crushed or ground into molding powder. Resins for protective coatings go to agitated thinning tanks and then are stored in tanks. And resins for latexes are stored in latex form.

In the polymerization reactor, the reaction may take place in a number of ways: 1) bulk polymerization, 2) solution polymerization, 3) suspension polymerization, or 4) emulsion polymerization. As their names imply, bulk polymerization occurs in the liquid or gaseous state. Solution polymerization proceeds in a solvent which is suitable for both monomer and catalysts. In suspension polymerization, the monomer is suspended in water by agitation and suspending agents such as, talc, Fullers earth, and bentonite. Emulsion polymerization adds soap to stabilize the monomer droplets and form aggregates called miscelles. The solvents, suspending agents, and emulsifying agents (soaps) are removed and recycled within the polymerization process. The method of polymerization used is determined by the manufacturer.

21.1 GENERAL CHEMISTRY

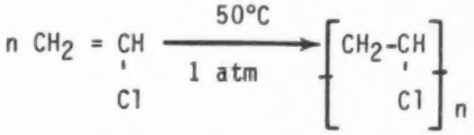
The chemistry of typical condensation and polymerization reactions is shown below:

a) condensation polymerization to make Nylon 66



$$n\ HOOC(CH_2)_4COOH + n\ NH_2(CH_2)_6NH_2 \xrightarrow[10\ atm]{270°C} \left[NH\underset{\underset{O}{\|}}{C}\ (CH_2)_4\ \underset{\underset{O}{\|}}{C}NH\ (CH_2)_6 \right]_n + 2nH_2O$$

b) addition polymerization to make polyvinyl chloride



$$n\,CH_2=\underset{Cl}{\underset{|}{CH}} \xrightarrow[1\text{ atm}]{50°C} \left[CH_2-\underset{Cl}{\underset{|}{CH}}\right]_n$$

The catalysts used to induce polymerization can be acidic substances, Ziegler-Natta catalysts, and various other initiators. The acidic substances used can be Bronsted acids, Lewis acids with co-initiators (water, methanol, acetic acid) or acidic solid surfaces such as in natural clays, synthetic zeolite, silica-alumina, or active carbon.

21.2 DESCRIPTION OF DISCHARGES

Releases from the polymerization processes occur as fugitive and particulate gaseous emissions, liquid wastes, and solid residues. The major sources of air contamination are: 1) the emissions of raw mateials or monomers, 2) emissions of solvents or other volatile liquids during the reaction, 3) emissions of sublimed solids (such as phthalic anhydride in alkyd resin production), and 4) emissions of solvents during storage and handling of thinned resins (USEPA, 1977). Wastewaters may emanate from within the process where it was required for the process operating conditions; or it may be formed during the course of chemical reactions; or it may be used in washdown of process vessels, area housekeeping, utility blowdown, and other sources such as laboratories (USEPA, 1974a). Solid residues will result from precipitates of separation and purification processes and bottoms products of distillation columns.

fugitive gaseous emissions - may occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains, and cooling towers.

reactants and solvent purification - gaseous releases may occur from fractionating columns and driers.
- liquid wastes may occur from caustic and water washes and driers.

	- emissions occur during storage and transport of monomers and solvents from vents in tanks and leaks in liquid transport.
reaction and product concentration	- reactants are released from vents on polymerization reactors. - effluent waters from centrifuges are contaminated with reactants and products. - solid effluents from settlers are disposed of.
blending and solvent removal	- addition of stabilizers may contaminate as the result of spillage. - solvent removal involves centrifuges, distillation columns, and liquid-liquid extraction which results in contaminated effluent waters, fugitive and intermittent air emissions, solid bottoms product, and liquid wastes containing extraction solvents.
drying and packaging	- air emissions occur from drying towers, baggers, and dust collectors. - solid residues are collected from screeners, which eliminate oversized particles, and as losses due to spillage - oil and grease are released from lubricating extruders.

Although most polymerizations are catalytic reactions, the catalysts are only recycled but not regenerated. The reactions do not occur in catalytic beds, instead the catalyst are introduced in solution or as a slurry. Not as much catalyst is required for a polymerization as is for other catalytic reactions. The catalysts are just used as initiators.

A characteristic of some polymerization processes is that the solid resins products are sold as pellets (chips), molding powder, protective coatings, or as latex resin. The treatment after polymerization varies with each use. No further wastes are generated if the resin is sold in latex form because no further processing is required. Protective coatings go to agitated thinning tanks which release a liquid waste caused by spills and washout. Resins for moldings are dried and crushed into molding powder which release air and solid emissions. Pellets are formed by drying and cutting usually in a screw-extruder and then passed through a dust collector and an oversized screener. The wastes occur as air emission, liquid wastes, and solid residues. The liquid wastes result because oil and grease used as lubricants are released. Solid residues result from the oversize screening process. Air emissions are released from the extruders and the dust collectors. Sometimes the pellets are processed further in a fiber spinning process. Air, liquid and solid emissions may occur.

Another characteristic of the polymerization processes is that monomers slowly polymerize in the pipelines, especially in the monomer recovery system pipelines. These lines must be cleaned out periodically, and the polymers are scrapped.

21.3 PRODUCTION PROCESS - POLYVINYL CHLORIDE BY POLYMERIZATION

Vinyl resins rank second in production to polyethylene. More emission data is available on the production of polyvinyl chloride (PVC) than polyethylene. Vinyl chloride monomer is one of the EPAs 129 priority pollutants; ethylene is not a priority pollutant. Therefore, the manufacturing process described in detail with emission points for this section will be the process for the manufacture of polyvinyl chloride by polymerization of vinyl chloride monomer: an addition reaction.

The production of polyvinyl chloride from vinyl chloride monomer is a batch process. Figure 21.1 shows a detailed flow diagram of a PVC suspension polymerization process. Seventy-nine percent of all PVC resins are made by suspension polymerization, 13% by emulsion polymerization, 6% by bulk polymerization, and 2% by solution polymerization (USEPA 1974b). Suspension polymerization is the most frequently used polymerization for all resins discussed in Section 21.0.

Although process schemes may vary, the processing sequence of the polymerization of polyvinyl chloride is generally 1) a polymerization step, 2) a separation step, and 3) a drying and packaging step. Liquid vinyl chloride monomer, water, a suspending agent, and a catalyst are added to a vigorously-stirred autoclave reactor. The slurried products proceed to a centrifuge where the water, unreacted monomer, and catalysts are drawn off and recycled. The PVC then passes through a drier which evaporates the water. The final step involves cutting into chips or pellets and screening to remove over-sized particles.

21.3.1 Polymerization Section

Vinyl chloride monomer, water, catalyst, and a suspending agent are added to the polymerizer. Most addition reactants are stored with an inhibitor to prevent polymerization from occurring in the storage tanks. The vinly chloride monomer does not normally contain an inhibitor. If an inhibitor is used, then it would have to be distilled off before reaching the reactor.

Suspension polymerization involves the mechanical dispersion of vinyl chloride in an aqueous medium with the aid of suspending agents. In a typical suspension process, the suspending agent is dissolved in water and added to the reaction vessel. The rest of the water, catalyst, and other additives, such as transfer agents, are then added. The reactor is sealed and evacuated, and vinyl chloride is added either by drawing into the evacuated reactor or by employing oxygen-free pressurized nitrogen to force the monomer into the reactor. The system is then closed and heated to

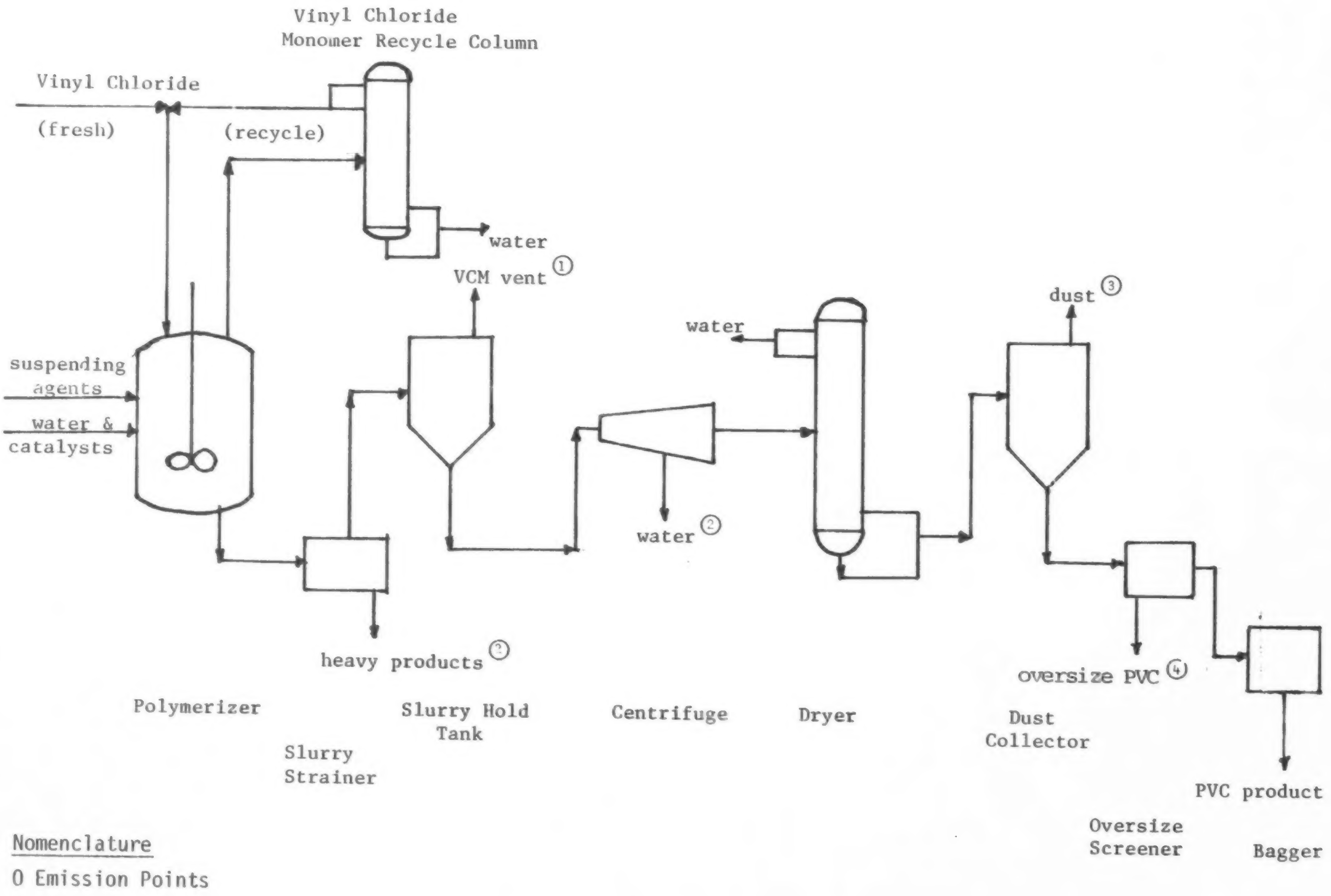


Figure 21-1

Process Flow Diagram for the Manufacture of Polyvinyl Chloride around 50°C. The tank is vigorously agitated throughout the entire reaction. The pressure increases to about 100 psi because of the temperature rise, and the polymerization is continued at a constant temperature until the pressure drops to about 10 to 20 psi as the result of monomer depletion (approximatley 72 hours). When the pressure drop occurs, the excess monomer is vented by compressing the reactor and the polymer batch is cooled and discharged to the slurry strainer. The excess monomer is recovered, condensed, and distilled before recycling to the reactor.

21.3.1.1 Emissions From Polymerization Section

USEPA (1974b) - Preliminary Assessment of the Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride - estimates that during vinyl chloride unloading, the normal atmospheric losses in disconnecting pipes, sampling, tank gauging, and losses from pump and compression seals to the tank cars should not be greater than 100 pounds per tank car. It also estimates that a 0.05% loss will result when charging the reactor from storage to polymerization. This includes losses from flanges and seals through all vinyl chloride handling equipment.

Vinyl chloride monomer is a gas at room temperature. After discharging the PVC, the reactor is full of a mixture of air, moisture, and vinyl chloride monomer at ambient conditions. Losses from the reaction kettles occur when they are opened, recharged, or sampled. PVC is released during reaction washout because PVC builds up on the walls of the reactor. No emissions were found to occur during reaction, unless the reactor was sampled. The monomer recovery section has the usual losses because of incomplete condensation and leaks in the distillation columns. The cooling water in the condensers will become contaminated from leaks in the system. An atmospheric emission of vinyl chloride will result when the nitrogen is vented. Fugitive emissions may result at valves, vents, seals and leaks in the distillation equipment in the monomer recycle section. Intermittent emissions may occur at relief vents on fractionation columns.

21.3.2 Separation Section

The separation section involves a slurry strainer, a slurry holding tank, and a centrifuge to separate out the residual vinyl chloride monomer, the catalysts, and the water. The suspended catalysts are removed in the settling tanks. The catalysts are soluble in the monomer but insoluble in water and PVC. Since there is only a small amount of monomer present, the catalysts settle out easily. The PVC can be separated from the water in a centrifuge. Since PVC is heavier than water, the water effluent discharged from the centrifuge contains very little PVC. The polymer product then proceeds to a dryer to remove any residual water.

21.3.2.1 Emissions from the Separation Section

A PVC loss of 0.1% was estimated by EPA (1974b) in the slurry strainer. Some residual monomer (0.1 - 0.5%) is drawn off from the slurry holding tank and vented to the air (USEPA, 1974b). A PVC loss of 0.1% was estimated to be emitted during the slurry holding tank washout after each batch operation. The water, catalysts and suspending agents are removed in the effluents of the centrifuge. This water will also be contaminated with PVC and residual vinyl chloride monomer. A PVC loss of 0.2% is estimated to be suspended in the water effluent. The amount of residual vinyl chloride monomer contaminating the centrifuge effluent water and being released from the slurry tank vent depends on how well the polymerizer was operated, i.e., was sufficient time allowed to complete the reaction, and was the reactor compressed and evacuated of vinyl chloride effectively.

21.3.3 Drying and Packaging

The residual water and vinyl chloride monomer are evaporated from the PVC in a dryer. It is a screw-extruder drier which cuts and dries the PVC into pellets. The PVC pellets pass through a dust collector which catches the smaller PVC particles and then an oversize screener (sifter) to catch the larger PVC particles. The final step is bagging the PVC chips or pellets in a product collector.

21.3.3.1 Emissions from Drying and Packaging

Emissions from the drying and packaging step occur in air emissions and solid residues. Unreacted vinyl chloride is emitted from the dryers and collected in the recovery system. It is separated from the water in the distillation columns in the recovery system. There are PVC losses from the dryer due to coalescence of the resin and periodic cleanout. This is almost entirely scrap. EPA (USEPA 1974b) estimates that an air emission of 0.2% of the total PVC amd 0.8% of the total residual vinyl chloride monomer results from the dust collectors. The oversized PVC removed in the sifter was estimated to be 0.3% of the total PVC and, unfortunately, 0.1% of the correct size PVC (USEPA 1974b). Both are solid residues and scrapped as off-grade material. In the product collectors, most plants use bag collectors so that the loss of resin is less than 1.0 pound/hour, but there are losses due to product changes which raise the total.

21.3.4 Other Releases

In addition to the above losses, others may occur due to bad batches, samples, polymer build-up, spillage, and incineration. Most plants experience 2 to 3 bad batches per month. These batches are either scrapped or sold as off-grade materials depending on the salvage value. Sampling occurs probably about 0.05% or 5 pounds per hour and is usually destroyed in testing. Vinyl chloride monomer slowly polymerizes in the pipelines, particularly in the recovery system pipelines. These lines must be cleaned out periodically, and the polymers are scrapped. Spillage occurs in bag filling and in bag breakage. When PVC or vinyl chloride monomer is incinerated without scrubbing, hydrogen chloride gas is emitted. It is estimated that 32,000 tons/yr of PVC is incinerated, with a consequent byproduct of 18,500 tons/yr of hydrogen chloride (USEPA 1975b). If the combustion is incomplete, vinyl chloride monomer is emitted. These releases cause acid rains when the hydrogen chloride combines with the moisture in the atmosphere.

21.3.5 Conclusion

Most of the vinyl chloride escapes directly to the atmosphere, with lesser amounts dissolved in water effluent streams and entrapped in sludge and solid wastes. PVC losses occur as particulates in air emissions, suspended solids in water effluents, and components of solid wastes. Figure 21.2 demonstrates the emission points and amounts emitted for the PVC process described. Table 21.2 tabulates these emissions. The total vinyl chloride monomer lost was 3 to 6.3% while PVC losses totalled 1.3%. USEPA (1977) estimates for the plastics industry that 17.5 kg/MT were particulate air emissions (PVC) and that 8.5 kg/MT were gaseous emissions (VC). The EPA also estimates that emissions of VC and PVC plants exceed 100 x 10^6 kg annually (USEPA 1975b). They estimate that approximately 90% of this emission comes from PVC plants.

Vinyl chloride levels in ambient air near PVC plants fluctuate sharply apparently due to opening of reactor vessels in the PVC plants, accidental plant discharge, variations in the production processes, and meteorological conditions. According to EPA, the average vinyl chloride concentration in the ambient air within 2 to 3 miles of the plant is 1 ppm (USEPA 1975b). The wastewater effluent from a PVC plant has a vinyl chloride monomer concentration of 2 to 3 ppm. The measured amount of vinyl chloride monomer in sludge/solid wastes from reactor vessels ranged from 100 ppm to 3000 ppm.

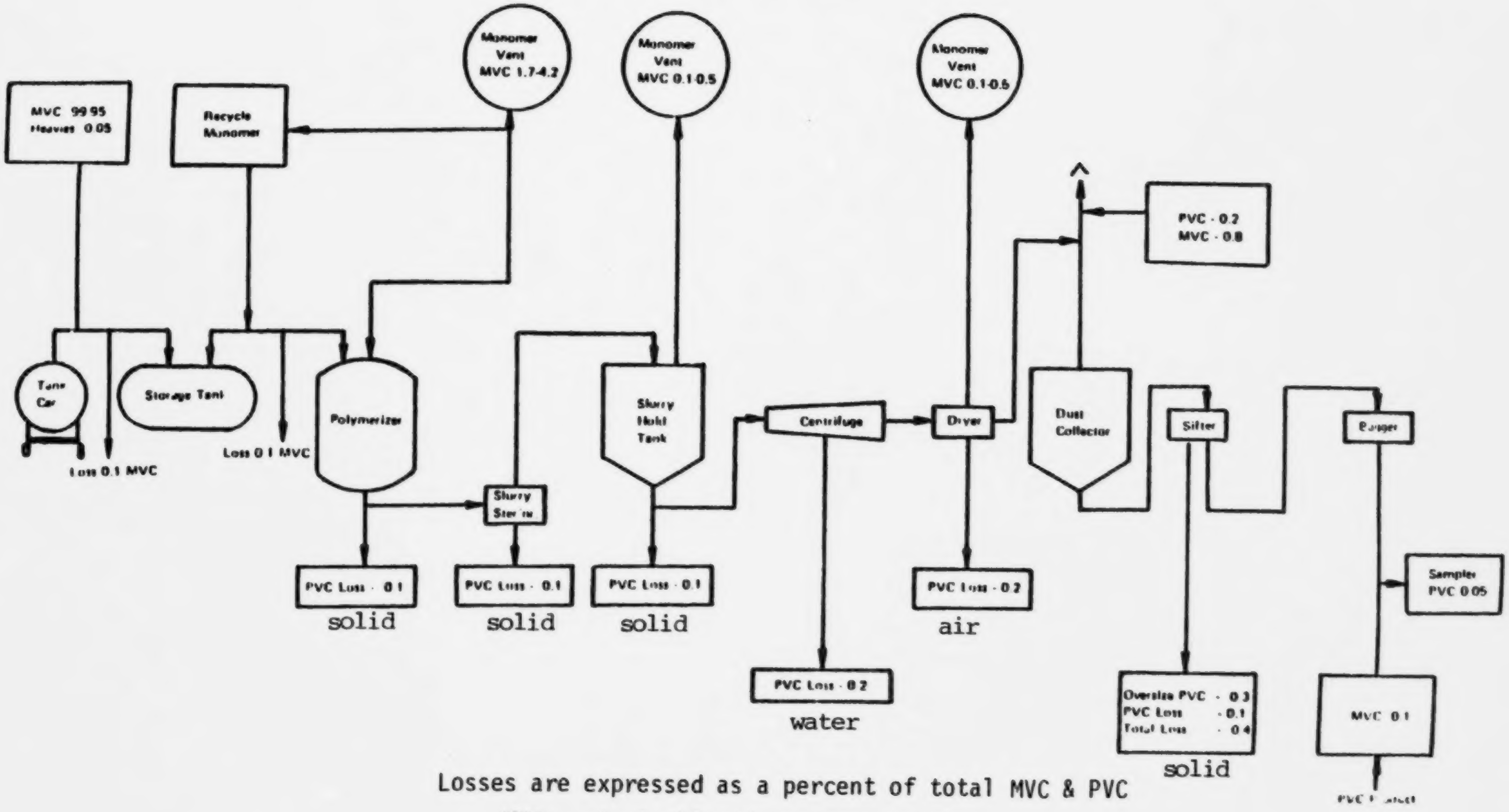
The foregoing analysis is an example of where emissions are most likely to occur from a polymerization process. The wastes will vary because of different operating conditions, volatilities and solubilities of the chemicals, and efficiency, age, and maintenance of equipment. Vinyl chloride monomer is extremely volatile. Every polymerization has different product cooling, purification, and separation trains.

21.4 SUMMARY OF EMISSION DATA

The process flow diagram for polyethylene-low density, polypropylene and polybutene are shown in Figures 21.3, 21.4 and 21.5 for comparison to the PVC flow diagram. These processes operate in gaseous, slurry, and

Figure 21-2

PRELIMINARY ESTIMATE OF LOSSES
IN PVC SUSPENSION POLYMERIZATION
(TYPICAL PROCESS)



Losses are expressed as a percent of total MVC & PVC

MVC: vinyl chloride monomer losses
total 3.0-6.3%

PVC: polyvinyl chloride losses
total 1.3%

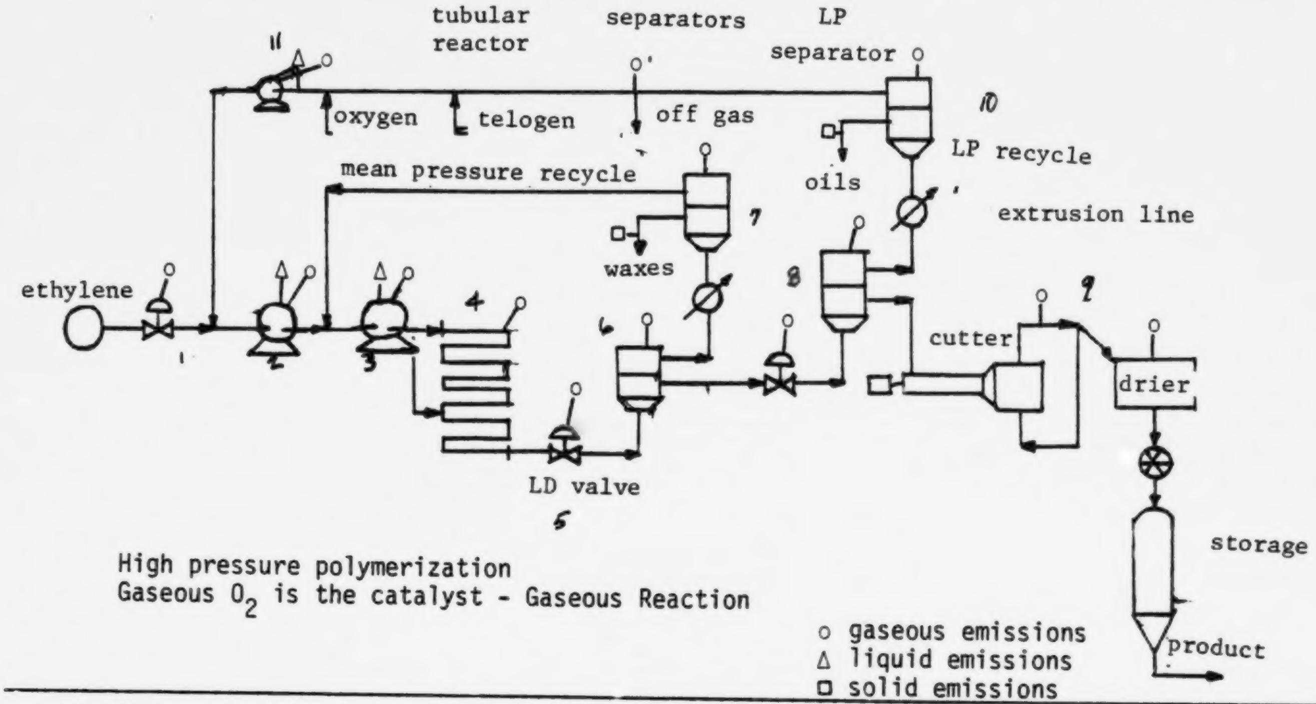
Source: USEPA, 1974b

TABLE 21-2. EMISSIONS FROM PVC MANUFACTURE
(IN PERCENT OF TOTAL VINYL CHLORIDE MONOMER USED AND POLYVINYL CHLORIDE PRODUCED)

	VCM Loss	PVC Loss
VCM tank car storage and handling and transfer to storage tanks	0.1% (air)	
VCM transfer from storage tank to polymerizer	0.1% (air)	
Loss from polymerizer	1.7-4.2% (air or recycled)	
Loss from polymerizer washout		0.1% (water)
Slurry strainer washout		0.1% (water)
Slurry hold tank monomer vent	0.1-0.5% (air)	
Slurry hold tank washout		0.1% (water)
Effluent from centrifuge		0.2% (water)
Dryer	0.1-0.5% (air)	0.2% (water)
Dust collector	0.8% (air)	0.2% (air)
Sifter		0.4% (solid)
Bagger	0.1% (air)	
Samples		0.05% (solid)
TOTAL	3.0 - 6.3%	1.3%

Source: Adopted from USEPA 1974b.

Figure 21-3
Process Flow Diagram for Polyethylene (Low Density)



High pressure polymerization
Gaseous O_2 is the catalyst - Gaseous Reaction

---

1 Ethylene, recycle ethylene, catalyst and chain transfer agents are mixed.

2 & 3 The reactants are compressed twice - first to 280 bars, then to 1800 bars.

4 The reactants pass to a jacketed-tubular reactor with 3 zones: preheating, reaction, and cooling

5 Special low-density valve to regulate pressure and flow.

6 Primary separator where the stream is split into medium and low pressure segments.

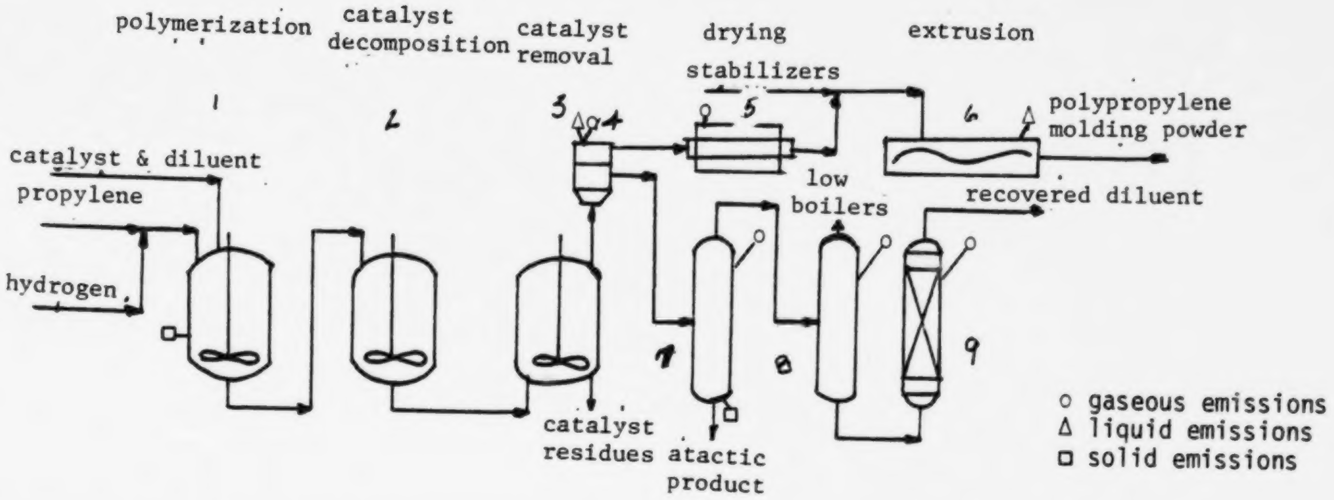
7 The medium pressure segment is mostly unreacted ethylene which is cooled and taken to wax separators before being recycled to compressors 3 .

8 The low pressure segment goes to the low pressure separator.

9 The condensed product from the low pressure separator proceeds to the extrusion line to be cut, dried, screened.

10 The residual gas from the low pressure separator is cooled and the waxes are separated. Catalysts and chain transfer agents are added before the gas is recycled back to the booster compressor 11 and 2 .

Figure 21-4
Process Flow Diagram for Polypropylene

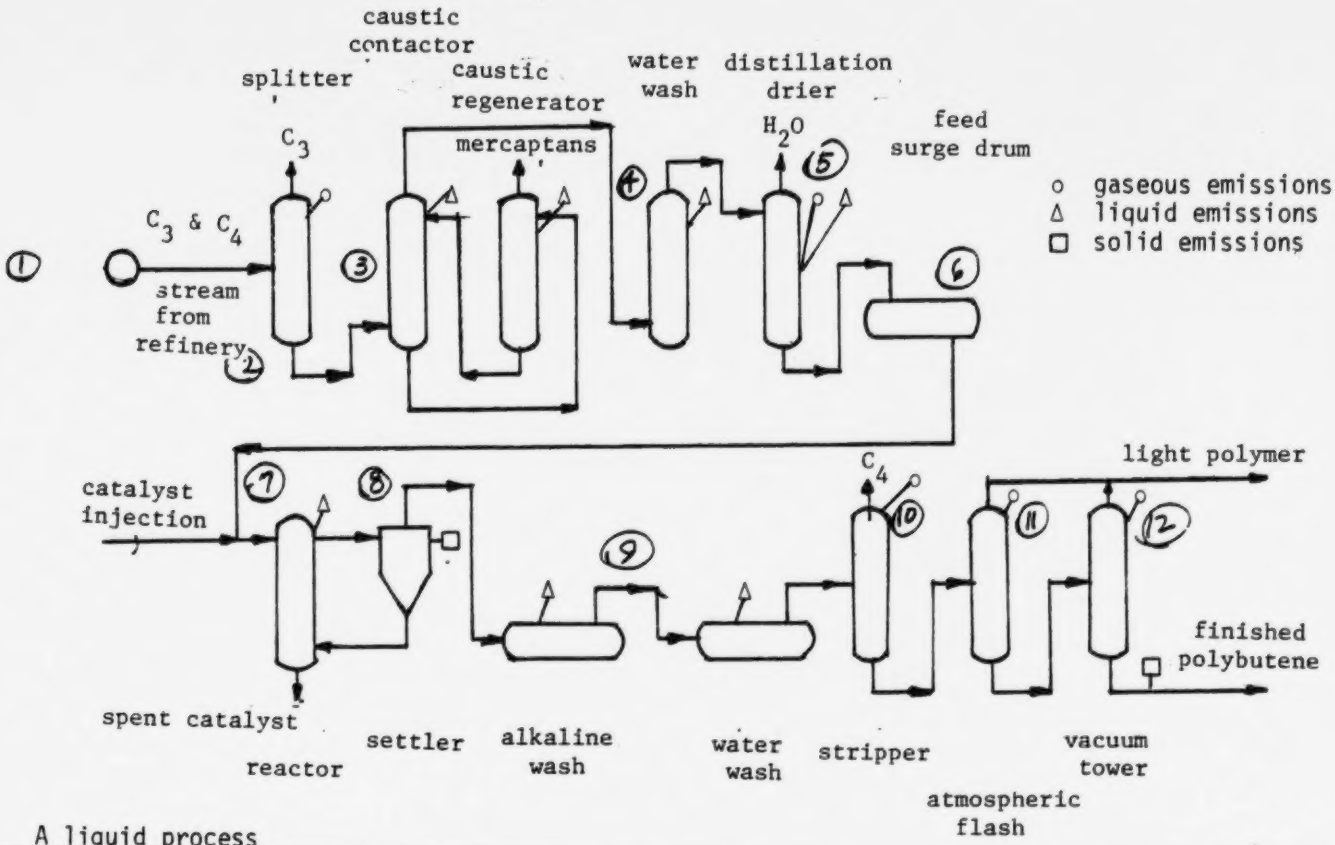


A slurry process in a hydrocarbon diluent using a titanium tetrachloride and an aluminumalkyl catalyst

---

1. Catalysts, hydrocarbon dilvent and purified propylene are continuously fed to the polymerization reactor operating at 50-100 C and 5-30 atm. Crystalline polypropylene is formed.
2. The polypropylene is insoluble and precipitates as a fine granular solid enveloping the catalyst particles. The catalysts are deactivated by dissolving in a solvent. (usually alcohol).
3. The solubilized catalysts are removed from the polymer-hydrocarbon phase in an extractor.
4. The polymer granules are separated from the bulk of the diluent in a centrifuge and then steam stripped and dried.
5. The polymer is then stabilized by addition of stabilizers.
6. The proplyene is extruded into molding pellets.
7. The hydrocarbon diluent is separated from the atactic product by evaporation of the solvent.
8. The diluent is then separated from the low boilers by solvent distillation.
9. The diluent is recovered and recycled.

Figure 21-5
Process Flow Diagram for Polybutenes



A liquid process

1 A mixed hydrocarbon stream is fed to the process - this stream contains C_4 olefins and paraffins, any C_3 and C_5 hydrocarbons and contaminants such as sulfur and water.

2 The reactants must be purified. First the C_3 and C_5 components are removed by distillation.

3 The reactants are treated for removal of mercaptans in a caustic contractor.

4 The reactants are water washed.

5 The reactants are then dried to remove the wash water.

6 The reactants are sent to a feed surge drum.

7 Aluminum chloride catalyst and purified reactants are fed to the polymerization reactor.

8 The products pass to a settler in which suspended catalyst is settled and returned to the reactor

9 The products proceed through an alkaline wash and a water wash for final removal of catalysts.

10 The final product consists of C_4 hydrocarbons, specification polybutenes and light polymers. The C_4 hydrocarbons are distilled off and used for other processing.

11 The products are then flashed at atmospheric pressure for removal of low boiling polymers and traces of butene.

12 The remaining light polymers are separated from the product in a vacuum stripper. The product is filtered and stored.

liquid media, respectively. No emission values were found; however points of emissions are demonstrated.

This section summarizes available emissions from polymerization processes. Table 21.3 shows major sources of emissions and estimated amounts by Hedley, et al. (1975). Most every chemical undergoing polymerization had been examined by Hedley et al. (1975). USEPA (1974a) Development Document for Synthetic Resins has grouped the wastewaters from several resins into subcategories. Table 21.4 shows what resins belong in which subcategory and also the limits for each subcategory.

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
unsaturated polyester	- propylene glycol	waste effluent to drain	by-product	r	water	21^1	NA	liquid	NA	NA
polycarbonate	- sodium chloride	pyridine recovery section azeotrope column waste to sewer	by-product	r	water	760^2	NA	liquid	NA	NA
	- raw materials solvents	during reaction	reactants	r	air	NA		gas	NA	NA
	- solvents resins	storage & handling	products	r	air	NA		gas	NA	NA
epoxy resins	- methyl isobutyl ketone	bottoms from reactor	by-product	r	land	45^3	NA	solid	NA	NA
	sodium chloride					344^3	NA	solid		
	sodium monohydrogen phosphate					16.7^3				
	epichlorohydrin-methanol					14.8^3				
	- epichlorohydrin	bottoms from epichlorohydrin dehydration column (drying towers)	reactant	r	land	NA	NA	solid	NA	NA
	- epichlorohydrin	steam ejector	reactant	r	air	NA	NA	gas	NA	NA
polypropylene	- ethane	polymer purification section	by-products	r	air	0.8^4	NA	gas	NA	NA
	propylene					20^4	NA	gas		
	propane	solvent still off gas				0.2^4	NA	gas		
	isopropyl alcohol & heptane					40^4	NA	gas		
styrene-butadiene* rubbers & plastics	- monomer, solvents sodium hydroxide	caustic wash for monomer	reactant	r	water	NA	NA	liquid	NA	NA

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES
(continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product
styrene-butadiene* rubbers & plastics (continued)	- solvents impurities	purge from steam strippers & solvent recovery section	reactants	r	air	NA	NA	gas	NA	NA
	- monomer solvent sodium hydroxide	polymer drying section	reactants	r	water	NA	NA	liquid	NA	NA
	- solvent vapors	polymer drying section	reactants	r	air	NA	NA	gas	NA	NA
styrene-acrylonitrile resins	- acrylonitrile	nitrogen purges on all reactors & equipment	reactants	r	air	trace^5	NA	gas	NA	NA
	styrene		reactants			trace^5	NA	gas	NA	NA
acrylonitrile-butadiene styrene resins	- styrene	serum from steam stripper in resin recovery section	reactions & by-products	r	water	trace^6	NA	liquid	NA	NA
	acrylonitrile					trace^6	NA	liquid		
	graft resin					8.8^6	NA	liquid		
	nacconal 90F					4.3^6	NA	liquid		
	calcium chloride					1.4^6	NA	liquid		
	- styrene	water wash on the rotary filter which separates coagulated resin from water	reactants & by-products	r	water	0.25^6	NA	liquid	NA	NA
	acrylonitrile					0.5^6	NA	liquid		
	sulfuric acid (98%)					0.25^6	NA	liquid		
	nacconal (90F)					2.5^6	NA	liquid		
	sodium bisulfite					0.25^6	NA	liquid		
	calcium chloride					0.75^6	NA	liquid		
	- acrylonitrile	steam stripper & decanter (recovery section for acrylonitrile)	reactant	r	water	trace^6	NA	liquid	NA	NA

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES
(continued)

Product	Pollutant	Location	Source	Type of Release *	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product
polystyrene (suspension)	- polystyrene	scrubber and centrifuges	product	r	water	20[7]	NA	gas	NA	NA
polystyrene (Bulk)	- polystyrene	rotary driers	product	r	air	trace[8]	NA	gas	NA	NA
	- polystyrene	process loss	product	r	air	21.8[8]	NA	gas	NA	NA
Polyethylene (Ziegler)	- ethylene	polymerization section	products & by-products	r	air	20[9]	NA	gas	NA	NA
	ethane					1[9]	NA	gas	NA	NA
	n-hexane	recycle compressor vent				22.5[9]	NA	gas		
	- methanol	polymer recovery section - methane column	by-products	r	air	trace[9]	NA	gas	NA	NA
(Ziegler or Phillips)	- suspend solids	400 gal. of wastewater/ ton of product		r	water	(100 ppm ton/ product)[10]	NA	liquid	NA	NA
	COD					(500-800 mg/l/ ton product)[10]	NA	liquid		
Polyethylene (LD) autoclave reactor	- ethylene	off-gas from autoclave reactor	by-products	r	air	42.6[11]	NA	gas	flare	No Info.
	ethane					1.05[11]	NA	gas		
	butane					2.15[11]	NA	gas		
	- COD	wastewater stream to drain 200 gal/ day/ton		r	water	(500-100mg/l)	NA	liquid	NA	NA
	oil					(100 mg/l)[11]	NA	liquid		
Polyethylene (LD) tubular reactor	- ethylene	off-gas from tubular reactor	by-products	r	air	30.8[11]	NA	gas	flare	NA
	ethane					0.9[11]	NA	gas		
	butane					1.6[11]	NA	gas		
	wax	water pollution	by-products	r	water	2.8[11]	NA	liquid	NA	NA

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES
(continued)

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Polyvinyl chloride or polyvinyl-vinylidene chloride	- vinyl chloride	vinyl chloride for reaction	reactant	r	air	40[12]	NA	gas	NA	NA
	- vinyl chloride	product drying section - recycle purification column	reactant	r	air	5[12]	NA	gas	NA	NA
	- BOD$_5$ COD suspended solids	wastewater loading will depend on the final processing steps 600-10,000 gal/ton product		r	water	0.1-48[12] 0.2-100[12] 1-30[12]	NA NA NA	liquid liquid liquid	NA	NA
polyvinyl acetate	- vinyl acetate	polymerization section reaction vent separator	reactants	r	air	1.5[13]	NA	gas	NA	NA
	- methanol	polymerization section feed dearator	by-product	r	air	0.5[13]	NA	gas	NA	NA
	- vinyl acetate hydroquinone	polymerization section inhibitor stripping column	inhibitor & reactants	r		20[13] 0.5[13]	NA NA		NA	NA
	- BOD$_5$ COD suspended solids	wastewater from coagulating & drying		r	water	0.2[13] 0-3[13] 0.2[13]	NA NA NA	liquid liquid liquid	NA	NA
polyvinyl alcohol	- methane acetiacid ethylacetate sodium sulfite	solvent & byproduct recovery section - ethyl acetate recovery column	solvents & by-products	r	water	0.5[14] 50[14] 25[14] 250[14]	NA NA NA NA	liquid liquid liquid liquid	NA	NA
amino resins urea-formaldehyde	- urea formaldehyde	waste & wastewater 216 gal/ton product		r	water	35[15] 35[15]	NA NA	liquid liquid	NA	NA
melamine-formaldehyde	- melamine formaldehyde	waste & wastewater 154 gas/ton product		r	water	20[16] 20[16]	NA NA	liquid liquid	NA	NA

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES
(continued)

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
Nylon 6	- low MW nylon 6	monomer recovery section-still bottoms	product	r	land	19^{16}	NA	solid	NA	NA
	- BOD_5 COD suspended solids	wastewater from washing and distillation steps (varies w/each phase)		r	water	$0.1\text{-}135^{16}$ $0.2\text{-}300^{16}$ $0\text{-}8^{16}$	NA NA NA	liquid liquid liquid	NA	NA
Nylon 66	- methanol nylon salt impurities (glutaric acid, succinic acid, 1,2-cyclohexadiamine)	nylon salt production - evaporator	solvents & by-products	r	water	2.6^{17} 4.0^{17} 1.55^{17}	NA NA NA	liquid liquid liquid	NA	NA
	- activated carbon nylon salt impurities	nylon salt purification and concentration adsorber	catalysts & by-products	r	land	15^{17} 3.15^{17} trace^{17}	NA NA NA	solid solid solid	NA	NA
	- hexamethylene-diamine	polycondensation - first stage reactor	catalysts	r	air	1.3^{17}	NA	gas	NA	NA
polychloroprene*	- catalyst residues acetic acid soap	wastestream from washing operations	catalysts & emulsifiers	r	water	NA	NA	NA	NA	NA
	- chloroprene	film drier	product	r	air	expected	NA	gas	NA	NA
polyethylene terephthalate	- ethylene glycol	cooler effluent	reactant	r	water	5.9^{18}	NA	liquid	NA	NA
	- ethylene glycol polyethylene glycol sodium hydroxide & sodium bisulfite	ethylene glycol purification column	by-products	r	land	0.48^{18} 23.1^{18} 0.1^{18}	NA NA NA	solid solid solid	NA	NA

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES
(continued)

						Uncontrolled Emissions			Controlled Emissions	
Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
	- ethylene glycol	glycol finishing column	by-products	r	land	1.9^{18}	NA	solid	NA	NA
	polyethylene glycol					0.1^{18}	NA	solid		
	misc. - both organic/inorganic					0.1^{18}	NA	solid		
polyacrylonitrile*	- acrylonitrile	monomer recovery sect.	reactants	r	air	NA	NA	gas	NA	NA
	acrylonitrile	vent to air & wastewater			water	NA	NA	liquid	NA	NA
	- solvent	fiber washing section solvent recovery	solvent	r	water	NA	NA	liquid	NA	NA
polyisoprene	- sodium hydroxide	water settlers from caustic wash	caustic	r	water	0.1^{19}	NA	liquid	NA	NA
	- isoprene dimer	solvent recovery column	by-products	r	water	NA	NA	liquid	NA	NA
	methanol	20,000 gal/hr of water from washing operations			water	NA	NA	liquid	NA	NA
	- solvent	drying section	solvent & by-product	r	air	2^{19}	NA	gas	NA	NA
	methanol					0.5^{19}	NA	gas		
polybutadiene	- sodium hydroxide and inhibitors	caustic wash	caustic & inhibitors	r	water	NA		liquid liquid	NA	NA
	- catalyst residues	expeller drier 300 gal/min of water	catalysts	r	water	25^{20}		liquid	NA	NA
	- solvent	air drier	solvent	r	air	5^{20}	NA	gas	NA	NA
ethylenes propylene copolymer (solution)	- catalyst residues	wash settler for catalyst removal (1500 gpm)	catalysts	r	water	50^{21}	NA	liquid	NA	NA

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES
(continued)

Product	Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity kg/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity kg/kkg product
	- hexane	water separator in solvent recovery section 9000 gph	solvent	r	water	30^{21}	NA	liquid	NA	NA
	- organic vapors (methane, ethylene propylene)	purge vents in solvent recovery section	by-products	r	air	6^{21}	NA	gas	NA	NA
	- hexane	driers	solvent	r	air	3^{21}	NA	gas	NA	NA
(suspension)	- catalyst residue	wash settler for catalyst removal (1,100 gph)	catalyst &	r	water	3.5^{21}	NA	liquid	NA	NA
	soap		reactants			4^{21}	NA	liquid	NA	NA
	sodium hydroxide		reactants		air	5^{21}	NA	liquid	NA	NA
	- toluene	drier	by-products	r	air	0.5^{21}	NA	gas	NA	NA
	- organic vapors (propylene, hexenes, hexane, toluene)	purge vents in monomer recovery section	by-products	r	air	30^{21}	NA	gas	NA	NA

TABLE 21-3 CHARACTERIZATION OF EMISSIONS FROM POLYMERIZATION PROCESSES
(continued)

Sources:

[1] Hedley (1974), p. 109. Based on 29,600 lb/12 hour batch.

[2] Ibid, p. 124. Based on 9100 kkg/yr capacity.

[3] Ibid, p. 139. Based on 9100 kkg/yr capacity.

[4] Ibid, p. 145. Based on 54,400 kkg/yr capacity.

[5] Ibid, p. 161. Based on 6800 kkg/yr capacity.

[6] Ibid, p. 169. Based on 13,600 kkg/yr capacity.

[7] Ibid, p. 169. Based on 29,500 kkg/yr capacity.

[8] Ibid, p. 170. Based on 29,800 kkg/yr capacity.

[9] Ibid, p. 176.

[10] Ibid, p. 177.

[11] Ibid, p. 187 & 188. Based on 90,700 kkg/yr capacity.

[12] Ibid, p. 202. Based on 22,700 kkg/yr capacity.

[13] Ibid, p. 204. Based on 22,700 kkg/yr capacity.

[14] Ibid, p. 206. Based on 13,600 kkg/yr capacity.

[15] Ibid, p. 215.

[16] Ibid, p. 227. Based on 13,600 kkg/yr capacity.

[17] Ibid, p. 239. Based on 13,600 kkg/yr capacity.

[18] Ibid, p. 247. Based on 37,700 kkg/yr capacity.

[19] Ibid, p. 289. Based on 45,400 kkg/yr capacity.

[20] Ibid, p. 298. Based on 45,400 kkg/yr capacity.

[21] Ibid, p. 313 & 315. Based on on 27,200 kkg/yr capacity.

*Hedley 1974. Qualitative data only.

+ Denotes that a release is routine (r) or accidental (a).

TABLE 21-4. TREATED WASTEWATER EFFLUENTS FOR POLYMERIZATION PROCESSES

Subcategory I	Subcategory II	Subcategory III	Subcategory IV
Polyvinyl chloride suspension emulsion bulk	cellophane rayon	polyester resin batch continuous	acrylic resins
	ABS/SAN	Nylon 66	
Polyvinyl acetate		Nylon 6	
Polystyrene suspension bulk		cellulose acetate	
Polypropylene			
Polyethylene low density high density			

Subcategory I - a low raw waste load: a raw waste load less than 10 units/1000 units of product.
- attainable low BOD_5 concentrations: less than 20 mg/liter.

Subcategory II - a high raw waste load: a raw waste load greater than 10 kg/kkg of product.
- attainable low BOD_5 concentrations.

Subcategory III - a high raw waste load.
- attainable medium BOD_5 concentrations: in the 30-75 mg/liter range.

Subcategory IV - a high raw waste load.
- attainable high BOD_5 concentrations: greater than 75 mg/liter.

REFERENCES

Hedley, W. H., S. M. Mehta, and C. M. Moscowitg, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Company, Inc.

Herrick, E. C., J. A. King, and R. P. Oullette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Kirk-Othmer. 1980. Encyclopedia of Chemical Technology, 3rd Ed. Volumes 4 and 9. New York, New York: John Wiley & Sons.

Shreve N. 1967. Chemical Process Industries, 3rd Ed. New York, New York: McGraw-Hill Book Company.

Sittig, M. 1975. Pollution Control in the Plastic and Rubber Industry. Park Ridge, New Jersey: Noyes Data Corporation.

U.S. EPA. 1974a. A Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Synthetic Resin Segment of the Plastics and Synthetic Materials Manufacturing Point Source Category. Washington, D. C.: U.S. EPA. Effluent Guidelines Division, Office of Air and Water Programs.

U.S. EPA. 1974b. Preliminary Assessment of the Environmental Problems Associated with Vinyl Chloride and Polyvinyl Chloride. Washington, D.C.: U.S. EPA.

U.S. EPA. 1975a. A Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Synthetic Polymer Segment of the Plastics and Synthetic Materials Manufacturing Point Source Category. Washington, D. C.: U.S. EPA. Effluent Guidelines Division, Office of Water and Hazardous Materials.

U.S. EPA. 1975b. Scientific and Technical Assessment Report on Vinyl Chloride and Polyvinyl Chloride. Research Triangle Park, N. C.: U.S. EPA, Office of Research and Development, Environmental Research Center.

U.S. EPA. 1977. Compilation of Air Pollutant Emission Factors, 3rd Ed. Research Triangle Park, N. C.: U.S. EPA, Office of Air and Water Management and Office of Air Quality Planning and Standards.

U.S. ITC. 1979. United States International Trade Commission. Synthetic Organic Chemicals. Washington, D.C.: U.S. Government Printing Office.

SECTION 22 - PYROLYSIS

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SECTION 22

PYROLYSIS

22.0 INTRODUCTION

Pyrolysis, also known as cracking, is the decomposition of chemical compounds by heat alone. Catalysts are not used; therefore, catalytic cracking is not included in this pyrolysis section. This section considers four types of cracking: thermal cracking, steam cracking, hydrocracking, and pyrolysis by electric arc. In thermal cracking, the reactants are passed through a chamber and heated to a high temperature. In steam cracking, the reactants are first diluted with steam, then heated for a fraction of a second and rapidly cooled. Hydrocracking is carried out in the presence of hydrogen at high pressure and at much lower temperatures. Pyrolysis by electric arc is when the heat required to breakdown the organic compounds is supplied by the current flowing through the electric arc.

Pyrolysis processes are generally similar. Each process includes a pyrolysis unit (some type of furnace) followed by a product cooling, purification, and separation. Figure 22-1 is a typical pyrolysis process diagram. The organic chemicals that are manufactured by pyrolysis are listed in Table 22-1.

22.1 GENERAL CHEMISTRY

Pyrolysis is the decomposition of chemical compounds by heat alone. Catalysts are not used in pyrolysis reactions. An example of pyrolysis occurs when ethane evolves hydrogen to form ethylene when heat is applied.

$$CH_3CH_3 \xrightarrow[760\text{-}870°C]{} CH_2{=}CH_2 + H_2(g) \qquad (1)$$

This is a widely used process in making polymer-grade ethylene. Another example is the formulation of melamine from urea which involves the evolution of water molecules.

FIGURE 22-1

A TYPICAL PYROLYSIS PRODUCTION PROCESS

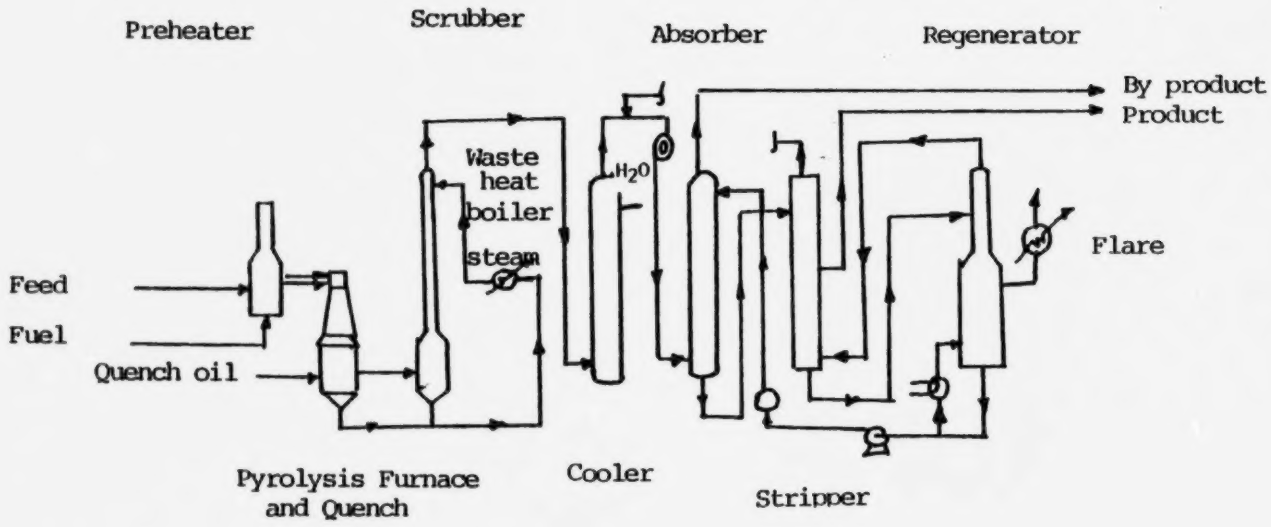


Table 22.1. ORGANIC CHEMICALS MANUFACTURED BY PYROLYSIS

Product	Amount kkg	Feedstock	Other Required Processes
Acetic anhydride	727,755^{2}	Acetic acid	Condensation
Acetylene	137,168^{2}	Light hydrocarbons	None
N-butyl acrylate	NA	Acetic acid	None
Cyanuric acid		Urea	None
Cyanuric acid Sodium dichloro isocyanurate Trichloro isocyanuric acid	NA^{3}	Caustic soda Chlorine Urea	Halogenation
Ethyl acetoacetate	NA^{3}	Acetic acid Ethanol	Esterification
Ethylene Propylene Hydrogen Pyrolysis gas	13,564,215^{1}	Butane Propane Ethane Naptha Gas oil	None
Hexachlorocyclopentadiene	NA^{3}	Pentane	Halogenation
Isoprene	248,560^{1}	Formaldehyde Hydrogen chloride Isobutylene	Condensation Hydrohalogenation
Ketene dimer (diketene)	NA^{3}	Acetic acid	None
Melamine	54,432^{2}	Urea	Condensation
Melamine		Dicyandiamide	Condensation
Methylacetoacetate	NA^{3}	Acetic acid Isopropanol	Esterification
Naphthalene	74,103^{1}	Coal tar Petroleum heavy aromatics	None
Oxalic acid	NA^{3}	Sodium formate	Condensation
Phenothiazine	NA^{3}	Diphenylamine Sulfur	None
Polyisocyanate	NA^{3}	Organic dichlorides Sodium cyanate	Polymerization

Table 22.1. ORGANIC CHEMICALS MANUFACTURED BY PYROLYSIS

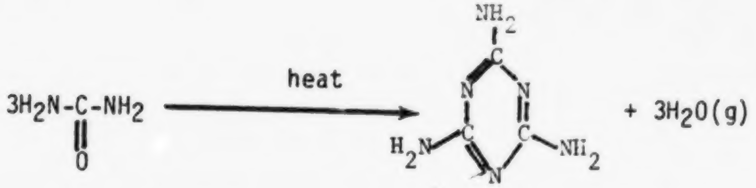
Product	Amount kkg	Feedstock	Other Required Processes
Propylene	6,440,359[1]	Propane Butane Naphtha Gas oil	None

Source: Herrick et al. 1979

[1] Source: USITC, Synthetic Organic Chemicals, 1979
Assumes 100% of products were made by pyrolysis

[2] Source: SRI, 1981
Assumes 80% of capacity is produced and also assumes the amount produced was by pyrolysis.

[3] Source: SRI, 1981
Does not give amounts produced, but lists producers.



(2)

By-products would include anything these chemicals could form as they were breaking down. For instance, by-products of ethylene production from butane includes hydrogen, methane, carbon dioxide, carbon monoxide, water, ethane, propane, propylene and acetylenes. The oxygen comes from impurities in the feed.

22.2 DESCRIPTION OF DISCHARGES

Releases from a typical pyrolysis process occur in wastewater, as fugitive gaseous emissions, and in solid residues.

fugitive emissions -	- occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains, and cooling towers (Wetherhold, et al., 1981).
pyrolysis section	- combustion gases from a gas-fired furnace - hydrocarbon and coke particulate emissions when decoking the furnace. - contaminated water from steam generation.
product cooling	- contaminated quench water or oil that comes in direct contact with the products in the quench towers. - contaminated cooling water from leaks in heat exchangers.
product purification	- product contaminants are removed by caustic scrubbers, oil scrubbers, gas scrubbers, or absorbers which will have liquid waste streams containing these contaminants. - gas scrubbers generally vent or flare pollutants to air.
separation of products and by-products	- strippers, fractionating columns; the undesired bottoms product will have to be disposed of or recycled.

cooling tower and boiler blowdown	-operation of the steam generation and cooling water systems produces the major portion of wastewater from pyrolysis units.

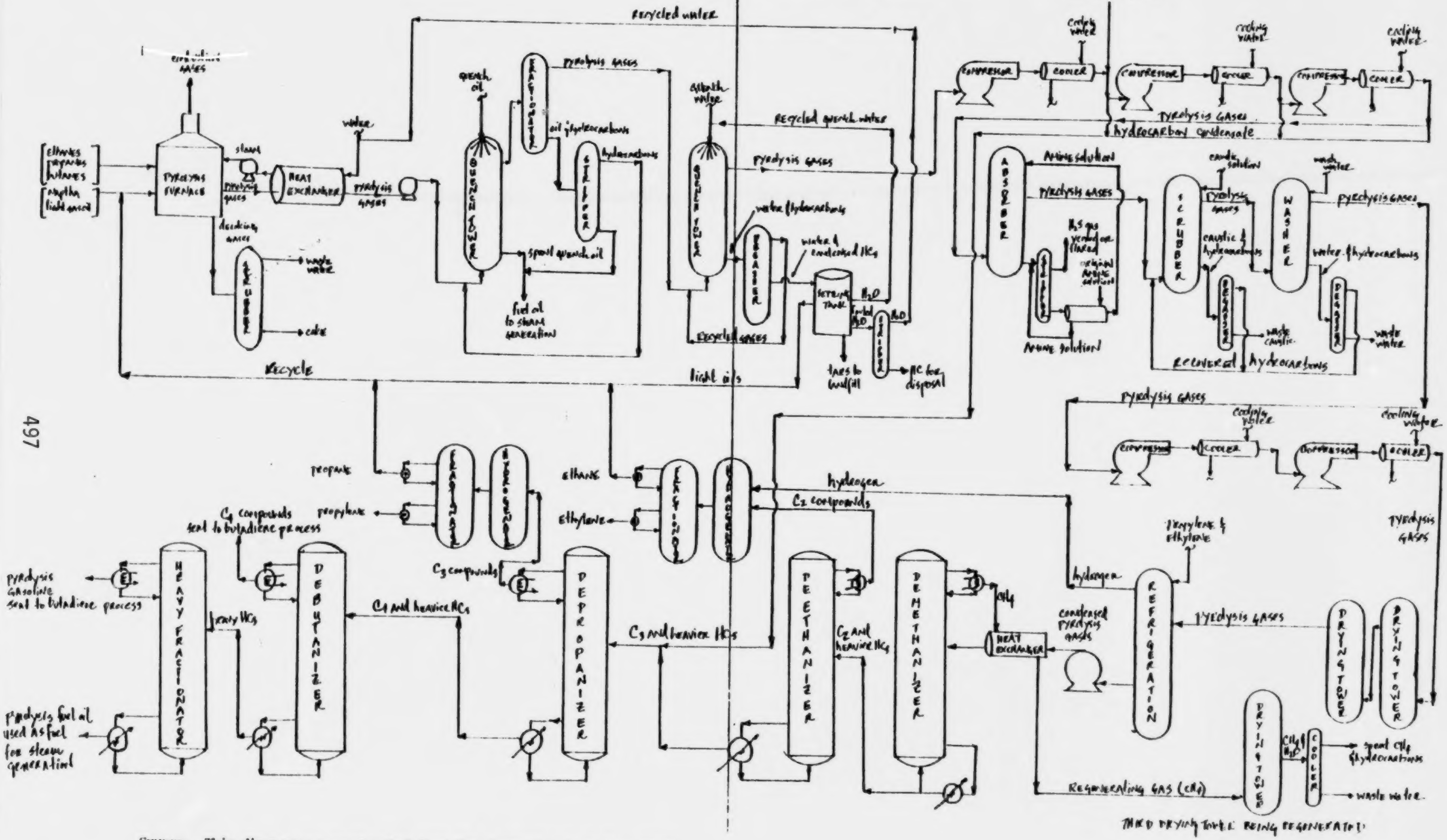
22.3 PRODUCTION OF ETHYLENE AND PROPYLENE BY PYROLYSIS

Ethylene and propylene are steam pyrolysis products from the olefins section of petrochemical industries. They have the highest production volume of all the organic chemicals considered for this pyrolysis section. Figure 22-2 is a detailed flow diagram of the ethylene pyrolysis process. The reactants are a hydrocarbon feedstream consisting of natural gas liquids such as ethanes, propanes, and butanes; naptha; and gas oil. The products are ethylene, propylene, butanes, fuel oil, pyrolysis gasoline, methane, and hydrogen. Typical ethylene product specifications after product separation and purification are shown in Table 22-2. Processing sequences may differ from company to company but generally they are: 1) thermal cracking, 2) oil quenching, 3) water quenching, 4) compression, 5) acid gas removal, 6) water removal, 7) demethanation, 8) C_2 separation, 9) C_3 separation, 10) C_4 separation, and 11) heavy fractionation. Following is a discussion of each process step including potential sources of emissions. The information was gathered from three references: Shreve 1967; Hydrocarbon Processing 1973; and Radian 1977.

22.3.1 Pyrolysis Furnace - Thermal Cracker

The decomposition of the reactants to pyrolysis products occurs in the thermal cracker. A hydrocarbon feedstream consisting of natural gas liquids, naptha, and gas oil is mixed with steam and heated in a tubular furnace to 1500-1600°F. Different feedstocks are cracked in separate furnaces when possible because they require different steam-to-hydrocarbon ratios for maximum production of ethylene. The heavier feedstocks such as naptha and gas oil almost always contain more impurities than the natural gas liquids, sulfur being the major impurity of environmental concern

FIGURE 22-2. FLOW DIAGRAM FOR ETHYLENE PRODUCTION



Source: This diagram was constructed from the discussion in Radian (1977).

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TABLE 22-2. ETHYLENE PRODUCT SPECIFICATIONS

Ethylene	99.90-99.95 mole %
Methane	0.01-0.1 mole %
Ethane	0.05-0.01 mole %
C_3 and heavier compounds	less than 10 ppm by weight
Acetylene	5-10 ppm by weight
Total sulfur	1-10 ppm by weight
Hydrogen sulfide	1 ppm by weight
Hydrogen	1 ppm by weight
Carbon monoxide	1-5 ppm by weight
Carbon dioxide	5-10 ppm by weight
Oxygen	2-5 ppm by weight
Water	5-10 ppm by weight

Source: Radian 1977

(Little, 1976). The tubular furnace consists of high temperature alloy of Ni-Cr steel tubes vertically hung between 2 fired sidewalls. The residence time is less than one second. The pyrolysis gases are quickly cooled in a tube and sheet heat exchanger that recovers the heat as high-pressured steam. The pyrolysis gases are then cooled further in an oil quench and/or a water quench. Pyrolysis gases from natural gas liquids only require a water quench.

22.3.1.1 Emissions from Thermal Cracking

Combustion gases from gas-fired furnaces may be fairly high in nitrate (NO_x) content because of high-flame temperature and non-stoichiometric combustion control (Radian 1977). Radian has estimated NO_x emissions to be 54 kg/hour for a 500-Gg/year ethylene plant. Sulfur emissions are low because most furnaces burn sulfur-free, plant-produced fuel.

Hydrocarbon and coke particulate emissions to the atmosphere occur when the furnaces are decoked. Coke burning is usually done once a month for several hours. Radian (1977) has reported that an average of 0.00001 kg of coke particulates per kilogram of ethylene produced are released. Some ethylene plants scrub decoking gases with water, creating an intermittent wastewater stream; other plants create an intermittent solid waste stream of coke which is landfilled.

22.3.2 Product Cooling - Oil Quenching

Pyrolysis gases from naptha and gas-oil feedstocks are rapidly cooled in an oil quench tower to retard secondary reactions. The pyrolysis gases enter the bottom of a vertical quench tower and come in direct contact with a countercurrent flow of quench oil. The pyrolysis gases then proceed to a fractionating column to remove the entrained oil, where as the overhead of the fractionating column they are pumped to a water quench. The bottoms of the fractionating column consist of oil with entrained hydrocarbons which is sent to a stripper where the entrained hydrocarbons are removed from the oil and recycled to the quench tower. The oil is recovered and used for steam generation.

22.3.2.1 Emissions from Oil Quenching

Radian (1977) has only reported that fugitive emissions may occur at fitting, valves, pumps, etc.

22.3.3 Product Cooling - Water Quenching

The pyrolysis gases from the natural gas liquid feedstock and the oil quench section are fed to a vertical water quench tower. Water quenching rapidly cools the pyrolysis gases. Again the flow is countercurrent and the pyrolysis gases come in direct contact with the quench water. The cooled pyrolysis gases exit the top of the quench tower and proceed to the compression section. The spent quench water is sent to a degasser to remove the entrained hydrocarbon gases. These gases are either vented, flared, or recycled back to the quench tower. The degassed water proceeds to settling drums where the condensed light oils settle out from the water. The light oils are sent back to the pyrolysis furnace. The water is recirculated to the quench tower. The bottom of the settling tank contains fouled condensate and tars. The tars are landfilled. The fouled condensate is cleaned in a stripper; this cleaned water is heated in the exchanger in the thermal cracking section to be reused as dilution steam in the pyrolysis furnace. The hydrocarbons removed in the stripper are sent to disposal. The stripper decreases the volume of oily water but not the total amount of hydrocarbons in the wastestream.

22.3.3.1 Emissions from Water Quenching

Radian (1977) reported that 19 Mg/hour of fouled condensate were generated from a 500 Gg/year ethylene plant and 3 Mg of hydrocarbons were gathered from the stripper at blowdown. The amount of tar extracted from the settling drums is dependent on the feedstock. Naptha feedstock generates 0.5 Gg/Gg of ethylene produced, and non-naptha feedstock generates 0.001 Gg/Gg of ethylene produced (Radian 1977). When degassing is practiced, continuous atmospheric emissions may result if the hydrocarbon gases are vented or flared.

22.3.4 Product Purification - Compression

The cooled pyrolysis gases are compressed in a series of 5 stages using single train centrifugal compressors. Intercoolers and gas-liquid separators are employed after each stage of compression. Intercoolers are water-cooled tubular heat exchangers that bring the compressed gases back down to their original temperature before compression. Some of the heavier hydrocarbons will inevitably condense. The condensed hydrocarbons will be isolated in gas-liquid separators and sent to the C_3 separation section. Refinery gases from crude distillation enter between the first and second compression stages, to prepare them so they can be separated as products in the following separation trains. The acid gas removal step is between the third and fourth stages of compression. After the 5th step, the compressed gases are sent to drying towers to have any water removed.

22.3.4.1 Emissions from Compressors

Polymer formation and fouling may occur, especially in the first 2 stages (Radian 1977). The compressors will be flushed with gas-oil to dissolve the polymeric materials formed. The frequency of intermittent compressor cleaning varies with the feedstock. Light hydrocarbon feedstocks require compressor cleaning once every 12 to 18 months (Radian 1977).

Fugitive emissions may result from compression, especially at the compressor seals. Radian (1977) reported an estimated loss of 0.000262 kg emitted per kg of ethylene produced from a gas oil feedstock. A water condensate stream containing dissolved hydrocarbons may be produced from compressor intercoolers.

22.3.5 Product Purification - Acid Gas Removal

The compressed pyrolysis gases contain acid gases, such as hydrogen sulfide, because they were formulated from sulfur containing feedstocks. The acid gases are removed by absorption followed by caustic scrubbing to a concentration of less than 10 ppm. In the absorption tower, the amine solution-containing ethanolamine sorbents has a temperature-dependent affinity for hydrogen sulfide. Hydrogen sulfide is absorbed from the pyrolysis gases to the ethanolamine sorbents and drawn off the tower. Then the contaminated ethanalomine sorbents are sent to a stripper where the temperature is raised and the hydrogen sulfide desorbs from the sorbents. The regenerated ethanolamine sorbents are recirculated through a heat exchanger and sent back to the absorption tower. The desorbed hydrogen sulfide gas is either vented or flared. Very few ethylene plants recover the sulfur; therefore, this hydrogen sulfide has a large pollution potential.

The pyrolysis gases are pumped to a caustic scrubber to remove any residual acid gases. The pyrolysis gases come in direct countercurrent contact with a caustic solution. The acid gases react with the caustic solution to form a precipitate and water, which fall to the bottom of the scrubber. The pyrolysis gases exit the top of the scrubber and are water washed. The spent caustic and spent wash water are degassed to remove hydrocarbon gases. The gases are vented, flared, or recycled while the spent caustic and wastewater are neutralized and ponded. The cleaned pyrolysis gases are compressed and sent to the drying towers.

22.3.5.1 Emissions from Acid Gas Removal

The hydrogen sulfide gas from the regenerated ethanolamine sorbents and from the neutralized caustic solution represents one of the biggest pollution potentials for ethylene plants (Radian 1977). Emissions of sulfur compounds have been reported as high as 0.0012 Mg SO_2/Mg of ethylene produced (Radian 1977). These emissions may also contain hydrocarbons.

The liquid waste stream from the caustic scrubber and water washing step is degassed, neutralized, and ponded. The degassing stream may be a continuous hydrocarbon emission. Radian (1977) estimates that the hydrocarbon emissions from the acid gas removal step are 0.00001 kg/kg of ethylene produced.

22.3.6 Product Purification - Water Removal

The last step of purifying the pyrolysis gases is to remove the water vapor. Dehydration is accomplished by adsorption on alumina or molecular sieves in packed columns. As the pyrolysis gases pass through two columns, the water vapor adsorbs to the molecular sieves. The dried pyrolysis gases then proceed to the product separation train. Meanwhile, a third column is being regenerated by heating. Regeneration is accomplished by passing an inert hot gas through the column while it is not in use. The regenerating gas is methane from the demethanation process. The hot regenerating gas collects the water vapor. The regenerating gases and water vapor contain hydrocarbons. They are cooled to condense the water vapor and heavier hydrocarbons. The water becomes a liquid waste stream since it contains hydrocarbons.

22.3.6.1 Emissions from Water Removal

As mentioned above, during regeneration of the drying towers, a small liquid waste stream is created and disposed. Treatment of this water is not known. Spent alumina or molecular sieves form a solid waste which is landfilled.

22.3.7 Product Separation - Demethanation

The pyrolysis gases are composed of hydrogen, methane, ethanes, propanes, butanes, and heavy oils. In order to separate the pyrolysis gases by fractionation, they must first be liquified. Therefore, the gases are passed through a refrigeration tower, which has a propylene-ethylene cascade, to condense the pyrolysis gases. The non-condensables, mostly hydrogen gas, are pulled off the top and sent to the hydrogenation unit in the C_2 separation step. The condensed pyrolysis gases are pressurized and cooled in heat exchangers and sent to the demethanizer tower. The demethanizer is a fractionation tower with an ethylene reboiler and a propylene condenser. The overhead product is methane. Methane is heated in the heat exchanger (prior to the demethanizer) and is used as the hot regenerating gas for regenerating the drying columns. The bottoms product, C_2 and heavier molecules, are sent to the deethanizer.

22.3.7.1 Emissions from Demethanation

Fugitive emissions of hydrocarbons may result from seals, valves, and leaks. Intermittent emissions may result from the relief vents on the fractionation towers. The entire fractionation train, which includes reboilers, condensers and distillation columns, emits an estimated 0.00050 kg of hydrocarbons/kg of ethylene produced (Radian 1977).

22.3.8 Product Separation - C_2 Separation

The C_2 compounds--ethanes, ethylenes, and acetylenes--are separated from the condensed pyrolysis products in a fractionating tower called the deethanizer. The deethanizer has a low pressure steam reboiler and a refrigerated propylene condenser. The C_3 and heavier compounds are taken off the bottom of the column and sent to the depropanizer. The overhead products, the C_2 compounds, are sent to a packed bed reactor for acetylene conversion by selective catalyic hydrogenation. Hydrogen is added to acetylene to make ethylene. The hydrogen is supplied by the refrigeration step in demethanation. Typically, 2 catalytic reactors are in parallel, so that one is on line while the other is being regenerated by heating. The C_2 compounds flow to a fractionation tower to separate ethane from ethylene. This tower has a propylene reboiler and condenser. The ethane is recycled back to the pyrolysis furnace, and the ethylene is compressed and condensed for sale.

22.3.8.1 Emissions from C_2 Separation

Fugitive emissions of hydrocarbons occur at seals, valves, vents, and leaks. Intermittent hydrocarbon emissions will result from relief vents in fractionating towers. The entire fractionation trains are estimated to release 0.0005 kg of hydrocarbons/kg of ethylene produced (Radian 1977).

When the acetylene converter catalysts are regenerated, a source of intermittent atmospheric emissions containing CO_2 and coke fines is created. The regeneration waste gases are scrubbed with water twice a year for a couple of days (Radian 1977). This scrubbing forms an intermittent liquid waste stream.

22.3.9 Product Separation - C_3 Separation

The purpose of C_3 separation is to isolate the propanes and propylenes from the deethanizer bottoms. C_3 separation incorporates three processes: depropanizing, catalytic hydrogenation, and fractionation of C_3 compounds. The depropanizer is a fractionating tower that separates the C_3 compunds from the heavier feedstocks. It has a steam reboiler and a water condenser. The bottoms products contain the heavier fraction, which is sent to further processing in the C_4 separation. The C_3 compounds are sent to a selective catalytic hydrogenation step in a packed-bed reactor which converts propadiene and methyl acetylene to propylene. These packed bed reactors are set up in parallel and regenerated as is the acetylene converter in the C_2 separation step. The C_3 compounds, propylene and propane, are then separated in a fractionating column with a steam reboiler and water condenser. The separation of propane from propylene is difficult because the boiling points are very close. The propylene is packaged for sale and the propane is recycled to the pyrolysis furnace.

22.3.9.1 Emissions from C_3 Separation

Fugitive emissions of hydrocarbons occur at valves, seals, and vents. Radian (1977) estimates that the C_3 separation train emits 0.0005 kg of hydrocarbons/kg of ethylene produced. Intermittent emissions occur at relief vents from the fractionation tower.

Catalyst regeneration causes intermittent atmospheric emissions of CO_2 and coke fines. If the regeneration gases are scrubbed with water, a liquid waste stream results.

22.3.10 Product Separation - C_4 Separation

In this step, the C_4 compounds are separated from the heavier feedstocks of the depropanizing bottoms in a fractionating column. The fractionating column has a steam reboiler and a water condenser. The overhead products which contain C_4 compounds are sent to the butadiene plant in the oil refinery. The bottoms products are sent to heavy fractionation.

22.3.10.1 Emissions from C_4 Separation

Fugitive emissions of hydrocarbons occur at seals, valves, and vents. Radian (1977) has estimated that this train will emit 0.0005 kg of hydrocarbons/kg of ethylene produced.

22.3.11 Product Separation - Heavy Fractionation

The heavy fraction from the debutanizer is composed of pyrolysis gasoline and pyrolysis fuel oil. These components are separated in a fractionating column with a steam reboiler and a water condenser. The pyrolysis gasoline is the overhead product and is sent to the butadiene process in the oil refinery. The pyrolysis oil, bottoms product, is used as fuel in steam generation.

22.3.11.1 Emissions from Heavy Fractionation

Fugitive emissions of hydrocarbons occur at vents, valves, and seals. Radian (1977) estimates that the fractionation train emits 0.00050 kg of hydrocarbons/kg of ethylene produced.

22.3.12 Other Releases - Flaring Gaseous Emissions

All emission gases are vented and then flared, except fugitive emissions. Leaks may occur at the valves, pumps, etc., from the ventilation system. Flaring may not be 100% efficient. If the burning is not complete, then emissions directly to the atmosphere will occur.

22.3.13 Other Releases - Cooling Tower and Boiler Blowdown

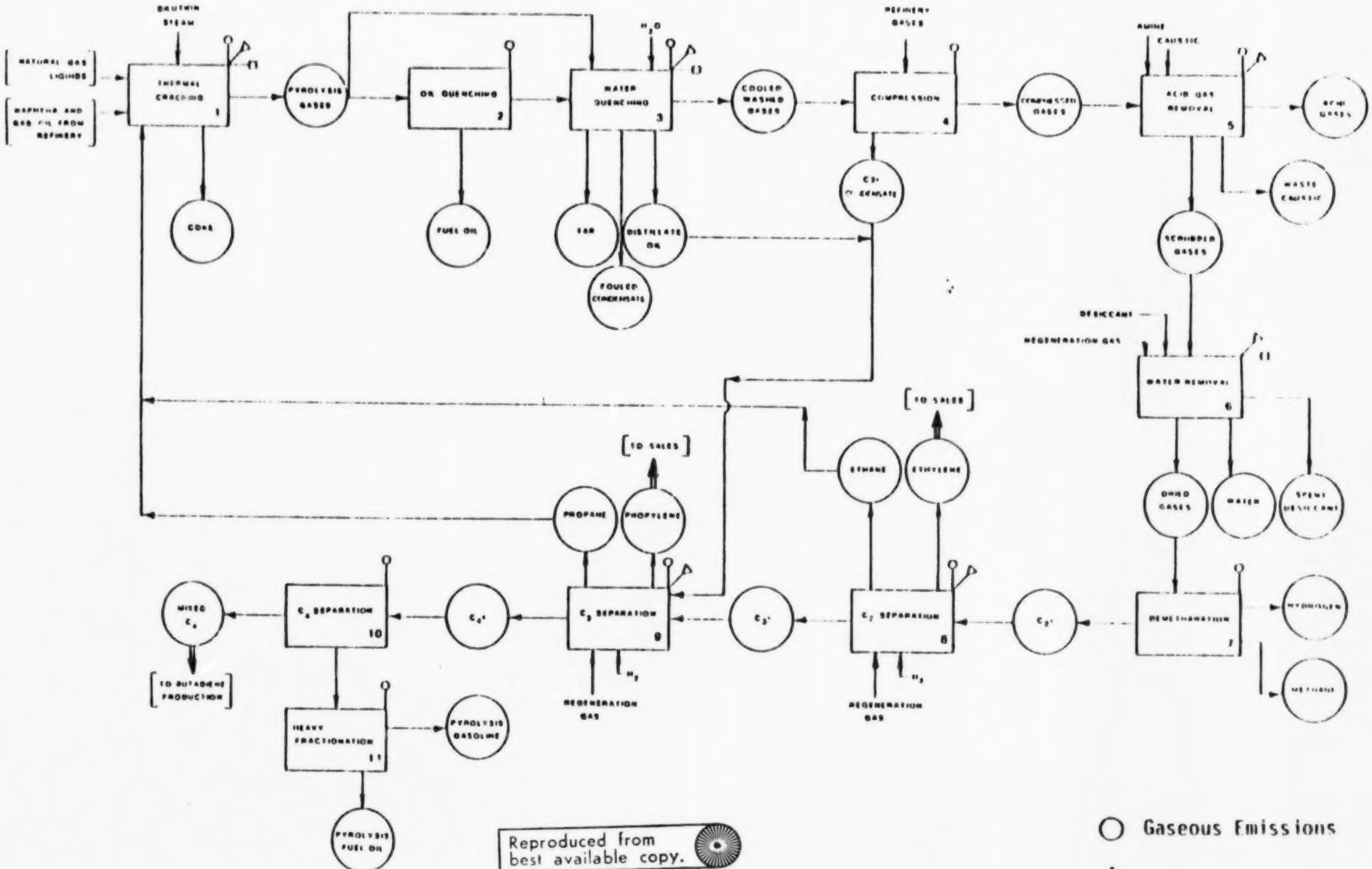
Hydrocarbon emissions may occur during cooling tower and boiler blowdown. These releases are estimated by Radian (1977) to be 45 kg/160 m^3 (100 lb/42,000 gal). Blowdown is when the oils which have built up in the cooling tower and boiler are recovered and disposed of. Another release occurs as the cooling water falls through the cooling tower. The gases will be emitted directly to the atmosphere at an estimated rate of 0.7 kg/1000 m^3 (60 lb/10^6 gal) (Radian 1977).

22.4 SUMMARY OF EMISSIONS DATA

Figure 22-3 summarizes the emissions and products from each step of ethylene production by pyrolysis. Table 22-3 is a summary of all the releases from each step to be used in conjunction with Figure 22-3. Table 22-4 presents releases from ethylene production utilizing different feedstocks. Table 22-5 shows the estimated amounts of releases that Radian (1977) calculated for a 227 Mg/year ethylene plant. A total of 4730 kg/day of hydrocarbons were estimated to be released. This estimation is for a plant which practices extensive hydrocarbon control.

Although these estimated emissions are for ethylene and propylene production, other organic chemicals undergoing pyrolysis will have similar equipment with similar wastes. Figure 22.4 is a process flow diagram for the production of acetylene with points of emissions outlined. No specific emissions data have been found for the acetylene pyrolysis or other pyrolysis processes. All processes will have a pyrolysis furnace; a product cooling, purification, and separation train; valves, pumps, etc.; cooling towers and steam generators similar to the ethylene plants. The wastes will vary because of different operating conditions, volatilities, solubilities, efficiencies, and maintenance of equipment. Basically, this description gives an example of where emissions are most likely to occur for a pyrolysis process.

FIGURE 22-3. ETHYLENE MANUFACTURE



○ Gaseous Emissions

△ Liquid Waste

☐ Solid Waste

Source: Radian, 1977.

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TABLE 22-3. SUMMARY OF EMISSIONS FROM AN ETHYLENE PLANT

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
- combustion gases high in NO_x content	thermal cracker combustion gases from gas-fired furnace	combustion gases	r	air	0.000095	54	gas	NA	NA
- hydrocarbon and coke particulates	when decoking the furnace	residual carbons	r	air	0.01	NA	gas	NA	NA
- hydrocarbon and coke particulates	scrubbing decoking gases	residual carbons	r	water	NA	NA	liquid	NA	NA
- residual coke	decoking the furnace	residual carbon	r	land	NA	NA	solid	NA	NA
- hydrocarbons	oil quench fugitive emissions at fittings, valves, pumps, etc.	products and by-products	r	air	NA	NA	gas	NA	NA
- hydrocarbons	water quench hydrocarbon gases from degasser maybe vented, flared, or recycled	by-products	r	air	NA	NA	gas	vented, flared or recycled	NA
- tars (naptha feedstock)	settling tank tars are landfilled	by-products	r	land	500	NA	solid	NA	NA
(non-naptha feedstock					1.0	NA	solid		
- hydrocarbons	fouled condensate stripper at blowdown	by-products	r	land	0.0006	0.34	solid	NA	NA
- hydrocarbons	compression fugitive emissions especially at compressor seals	by-products	r	air	0.262	NA	gas	NA	NA
- hydrocarbons	cooling water in intercoolers	by-products	r	water	NA	NA	liquid	NA	NA
- hydrocarbons	from flushing compressors	by-products	r	water	NA	NA	liquid	NA	NA

TABLE 22-3. SUMMARY OF EMISSIONS FROM AN ETHYLENE PLANT (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
	acid gas removal								
- hydrogen sulfide gas	from stripper after absorber	contaminants	r	air	1.2 SO_2	NA	gas	NA	NA
- hydrocarbons	for entire acid gas removal step	by-products	r	air	0.01	NA	gas	NA	NA
- caustic and hydrocarbons	spent caustic and wastewater from scrubber and water wash	solvents and by-products	r	water	NA	NA	liquid	neutralized and ponded	NA
	water removal								
- regenerating gas contaminated with hydrocarbons	spent regenerating gas from regenerating dryers	by-products	r	air	NA	NA	gas	NA	NA
- hydrocarbons	wastewater from cooling after regenerating	by-products	r	water	NA	NA	liquid	NA	NA
- spent alumina or molecular sieves	packing for packed beds are disposed after useful life is completed	packing	r	land	NA	NA	solid	NA	NA
	demethanation								
	C_4 separation								
	heavy fractionation								
- hydrocarbon	fugitive emissions may occur at seals, valves, and leaks from each distillation column	by-products	r	air	0.5/column	NA	gas	NA	NA
- hydrocarbon	intermittent emissions from relief vents on fractionation towers	by-products	r	air	NA	NA	gas	NA	NA

TABLE 22-3. SUMMARY OF EMISSIONS FROM AN ETHYLENE PLANT (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg product
	C_2 and C_3 separation								
- CO_2 and coke fines	same emissions as demethanation when regenerating catalyst beds from hydrogenation	by-products	r	air	0.5	NA	gas	NA	NA
- hydrocarbons and catalyst fines	Intermittent liquid wastestream from scrubbing rengeneration waste gases	by-products	r	water	NA	NA	liquid	NA	NA

Source: Adapted from Radian (1977). Based on 200,000 kkg/yr capacity.

+Indicates that release is routine (r).

TABLE 22-4 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE MANUFACTURING PROCESS

Pollutant	Location	Source	Type of Release +	Receiving Medium	Uncontrolled Emissions Quantity g/kkg product	Uncontrolled Emissions Rate kg/hr	Uncontrolled Emissions Form	Controlled Emissions Control Technology	Controlled Emissions Quantity g/kkg
Benzene	Compressor lube-oil vents	feedstock	r	air					
	Single compressor trains				0.0348	0.0009	gas	none	
	Dual compressor trains				0.0018				
	Other normal process emissions							none	
	Intermittent emissions							flares	
	Single compressor trains				29.8	0.77			.6-3.0
	Dual compressor trains				3.8	0.099			.08-.38
	Fugitive		a	air	8.3	0.21		correction of leaks	1.58
Total VOC	Compressor lube-oil vents	feedstock & by-product	r	air			gas	none	
	Single compressor trains				13.9	0.36			
	Dual compressor trains				27.8	0.72			
	Other normal process emissions				27.6	0.71		none	
	Intermittent emissions							flares	
	Single compressor trains				6910	179.0			138-691
	Dual compressor trains				1506	39.0			30-151
	Fugitive		a	air	3608	9314		correction of leaks	690

Source: White 1980, Vol. 9. Feed composition is 100% ethane. Based on 226,800 kkg/yr.

TABLE 22-4 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity g/kkg product	Rate kg/hr	Form	Control Technology	Quantity g/kkg
Benzene	Compressor lube-oil vents	feedstock	r	air					
	Single compressor trains				0.193	0.0120	gas	none	
	Dual compressor trains				0.386	0.0240			
	Other normal process emissions							none	
	Intermittent emissions								
	Single compressor trains				733.2	45.6		flares	14-73
	Dual compressor trains				93.6	5.8			1.9-9.4
	Fugitive		a	air	44.5	2.8		correction of leaks	8.5
Total VOC	Compressor lube-oil vents	feedstock & by-product	r	air			gas	none	
	Single compressor trains				5.79	0.36	gas	none	
	Dual compressor trains				11.60	0.72			
	Other normal process emissions				72.0	4.47		none	
	Intermittent emissions								
	Single compressor trains				11,690	726.0		flares	234-1169
	Dual compressor trains				2,114	131.3			42-211
	Fugitive		a	air	1,450	90.1		correction of leaks	277

Source: White 1980, Vol. 9. Feed composition is 100% naptha. Based on 544,200 kkg/yr capacity.

TABLE 22-4 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity g/kkg product	Rate kg/hr	Form	Control Technology	Quantity g/kkg
Benzene	Compressor lube-oil vents	feedstock	r	air					
	Single compressor trains				0.160	0.0124	gas	none	
	Dual compressor trains				0.320	0.0248			
	Other normal process emissions							none	
	Intermittent emissions								
	Single compressor trains				791.9	61.5		flares	15.8-79.2
	Dual compressor trains				101.1	7.9			2.0-10-1
	Fugitive		a	air	36.8	2.85		correction of leaks	7.0
Total VOC	Compressor lube-oil vents	feedstock & by-product	r	air			gas	none	
	Single compressor trains				4.64	0.36			
	Dual compressor trains				9.28	0.72			
	Other normal process emissions				80.4	6.24		none	
	Intermittent emissions								
	Single compressor trains				12,314	956.2		flares	246-1231
	Dual compressor trains				2,195	170.5			44-220
	Fugitive		a	air	1,168	90.7		correction of leaks	223

Source: White 1980, Vol. 9. Feed composition is 50% naptha and 50% gas oil. Based on 680,300 kkg/yr capacity.

TABLE 22-4 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity g/kkg product	Rate kg/hr	Form	Control Technology	Quantity g/kkg
Benzene	Compressor lube-oil vents	feedstock	r	air					
	Single compressor trains				0.206	0.0128	gas	none	
	Dual compressor trains				0.412	0.0256			
	Other normal process emissions							none	
	Intermittent emissions								
	Single compressor trains				851.4	52.9		flares	17.0-85.1
	Dual compressor trains				108.7	6.8			2.2-10-9
	Fugitive		a	air	47.4	2.9		correction of leaks	9.1
Total VOC	Compressor lube-oil vents	feedstock & by-product	r	air			gas	none	
	Single compressor trains				5.79	0.36			
	Dual compressor trains				11.60	0.72			
	Other normal process emissions				88.8	5.51		none	
	Intermittent emissions								
	Single compressor trains				12,968	805.6		flares	259-1297
	Dual compressor trains				2,278	141.5			44-228
	Fugitive		a	air	1,466	91.1		correction of leaks	281

Source: White 1980, Vol. 9. Feed composition is 100% gas oil. Based on 544,200 kkg/yr capacity.

TABLE 22-4 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity g/kkg product	Rate kg/hr	Form	Control Technology	Quantity g/kkg
Benzene	Compressor lube-oil vents	feedstock	r	air			gas	none	
	Single compressor trains				0.159	0.00288			
	Dual compressor trains				0.318	0.00576			
	Other normal process emissions							none	
	Intermittent emissions								
	Single compressor trains				116.3	2.1		flares	2.3-11.6
	Dual compressor trains				14.9	0.27			.30-1.5
	Fugitive		a	air	36.7	0.66		correction of leaks	7.0
Total VOC	Compressor lube-oil vents	feedstock & by-product	r	air			gas	none	
	Single compressor trains				19.9	0.36			
	Dual compressor trains				39.7	0.72			
	Other normal process emissions				39.6	0.72		none	
	Intermittent emissions								
	Single compressor trains				7822	141.7		flares	156-782
	Dual compressor trains				1621	29.4			32-162
	Fugitive		a	air	4935	89.4		correction of leaks	943

Source: White 1980, Vol . 9. Feed composition is 50% ethane and 50% propane. Based on 158,700 kkg/yr capacity.

TABLE 22-4 CHARACTERIZATION OF EMISSIONS FROM THE ETHYLENE MANUFACTURING PROCESS (continued)

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity g/kkg product	Rate kg/hr	Form	Control Technology	Quantity g/kkg
Benzene	Compressor lube-oil vents	feedstock	r	air			gas	none	
	Single compressor trains				0.187	0.00483			
	Dual compressor trains				0.374	0.00966			
	Other normal process emissions							none	
	Intermittent emissions								
	Single compressor trains				235.8	6.1		flares	4.7-23.6
	Dual compressor trains				30.1	0.78			0.6-3.0
	Fugitive		a	air	43.0	1.11		correction of leaks	8.2
Total VOC	Compressor lube-oil vents	feedstock & by-product	r	air			gas	none	
	Single compressor trains				13.94	0.36			
	Dual compressor trains				27.8	0.72			
	Other normal process emissions				51.5	1.33		none	
	Intermittent emissions								
	Single compressor trains				8460	219.0		flares	169-846
	Dual compressor trains				1704	44.1			34-170
	Fugitive		a	air	3295	85.3		correction of leaks	630

Source: White, 1980, Vol. 9. Feed composition is 100% propane. Based on 226,800 kkg/yr capacity.

Table 22-5. ESTIMATED HYDROCARBON LOSSES FROM AN ETHYLENE PLANT PRODUCING 227 Gg (500 MILLION LB)/YR[a]

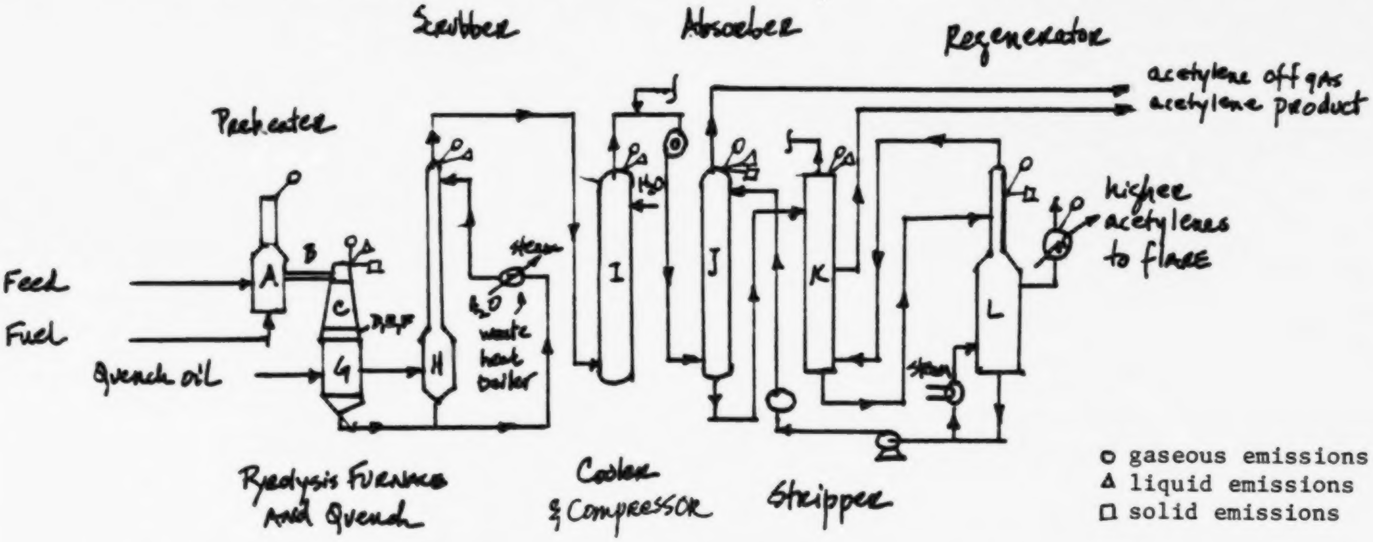
Source	Loss Factor		Estimated Emissions kg/day	(lb/day)
Valves	68g	(0.15 lb)/day/valve	306	675
Pumps (mechanical seals)	1.5 kg	(3.2 lb)/day/seal	218	480
Compressors (centrifugal, mechanical seal)	1.5 kg	(3.2 lb)/day/seal	29	64
Compressors (reciprocal, packed seal)	2.5 kg	(5.4 lb)/day/seal	2	5
Cooling Water	0.7 kg/1000 m^3	(60 lb/10^6 gal)	195	430
Process Drains and Wastewater Separations	68.1 kg/160 m^3	(150 lb/42,000 gal) capacity	1400	3000
Blowdown	45 kg/160 m^3	(100 lb/42,000 gal) capacity	900	2000
Relief Valves on Operating Vessels	1.3 kg	(2.9 lb)/day/valve	522	1150
Miscellaneous Losses	4.5 kg/day/160m^3	(10 lb/day/42,000 gal) capacity	90	200
Storage Vessels			1100	2400
	Total		4730	10430

[a] These data apply to plants practicing extensive hydrocarbon control.

Source: Radian 1977.

Figure 22-4

Pyrolysis to Acetylene by Partial Oxidation from Hydrocarbon Feedstock



Partial combustion of natural gas

A Oxygen and natural gas are preheated to 1200 F, using fuel gas in preheater.

B The two hot gases are conducted to and mixed in a burner in a molar ratio of 0.6 : 100(oxygen : methane).

C The burner consists of three parts: mixing chamber, flame or chemical conversion zone, followed by quench chamber with quench oil or water spray.

D The chemical conversion is almost instantaneous, with partial combustion of CH_4 (2/3).

E Overall reaction of CH_4 is 90 - 95%, whereas O_2 is 100% converted.

F Residence time is 0.001 to 0.01 second.

G The acetylene and gases are cooled rapidly by quench oil or water spray to 100 F and have the following composition: Acetylene (8.5%), Hydrogen (57.0%), Carbon monoxide (25.3%), Carbon dioxide (3.7%), Methane (4.0%), Higher Acetylenes (0.5%) and Inerts (1.0%).

H The soot is removed by carbon filter, i.e. the higher acetylenes.

I The clean gases are compressed to 165 psig.

J Acetylene is removed in a packed column by selective solvent (dimethyl formamide).

K Carbon dioxide is flashed and stripped overhead out of the rich solvent in a packed column, where the acetylene is fractionated out, giving a +99% product with a 30 to 36% yield on the carbon in the natural gas.

L Higher acetylenes and water are stripped out under reduced pressure and the solvent reused.

Source: Hydrocarbon Processing 1973.

REFERENCES

Hedley, W. H., S. M. Mehta, and C. M. Moscowitz, et al. Monsanto Research Corporation. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Co., Inc.

Herrick, E. C., J. A. King, and R. P. Ouellette. 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Little, A. D., Inc. 1976. Environmental Consideration of Selected Energy Conservation Manufacturing Process Options. Vol. 1. Industry Summary Report. Cincinnati, Ohio: Industrial Environmental Research Lab.

Morrison, R. T., and R. N. Boyd. 1976. Organic Chemistry, 3rd ed. Boston, Massachusetts: Allyn and Baron, Inc. pp. 110-111.

Radian Corp. 1977. Industrial Process Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Research Triangle Park, North Carolina: Industrial Environmental Research Lab, U.S. EPA.

Shreve, R. N. 1967. Chemical Process Industries, 3rd ed. New York, New York: McGraw-Hill Book Company.

Sittig, M. 1962. Organic Chemical Processes. Pearl River, New York: The Noyes Press, Inc. p. 12.

Sittig, M. 1978. Petroleum Refining Industry Energy Saving and Environmental Control. Park Ridge, New Jersey: Noyes Data Corporation.

Wetherold, R. G., D. D. Rosebrook, and B. A. Tichenor. 1981. Assessment of Atmospheric Emissions from Petroleum Refining. Research Triangle Park, North Carolina: U. S. Environmental Protection Agency.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 9. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, N. C. EPA-450/3-80-028d.

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SECTION 23

REFORMING (STEAM) - WATER GAS REACTION

23.0 INTRODUCTION

The only product made by the reforming (steam) - water gas reaction is methanol, and 99% of all methanol is made by this process. There are variations in pressure, reactants, and catalysts used to make methanol, but all variations basically employ the same process sequence. Table 23-1 lists the various pressures and reactants used to produce methanol and amounts produced in 1980. Notice that there are two processes, high pressure and low pressure, and three different reactants, natural gas, naphthalene, and liquified petroleum gas. The most commonly used reactant is natural gas (methane) (White 1980).

The reforming (steam) - water gas reaction refers to reacting steam and methane to make water gas (which consists of carbon monoxide, hydrogen, and carbon dioxide) and then converting water gas into methanol. Figure 23-1 is a generalized flow diagram of the reforming (steam) - water gas reaction. Although process schemes may vary, generally they consist of (1) desulfurization of reactants, (2) steam reforming of natural gas, (3) compression, (4) synthesis of methanol in a catalytic converter, (5) cooling and condensing products, and (6) distillation for purification. Equipment would differ because higher pressures would require more compressors, impure feedstreams would need more purification (desulfurization), and different reactants would first have to be converted to methane by one of the other 23 processes discussed in this report.

23.1 GENERAL CHEMISTRY

The reforming (steam) - water gas reaction is a two-step gaseous reaction. In the first step, high-pressure steam reacts with methane to form carbon monoxide, carbon dioxide, and hydrogen, as shown in reactions (1) and (2). This is called steam reforming. The reactions take place in

TABLE 23-1. REFORMING STEAM-WATER GAS PRODUCTS AND THEIR MANUFACTURE IN 1980

Products	Amount^a kkg	Feedstock	Other Required Processes
Methanol^b	1,276,000	Naphtha	None
Methanol^b		Natural Gas	None
Methanol^c	2,850,000	Naphtha	None
Methanol^c		Natural Gas	None
Methanol^c		Liquified Petroleum	None
Methanol^c		Naphtha	
Dimethyl Ether		Carbon dioxide	

Total 4,126,000

Source: Herrick, et al. 1980

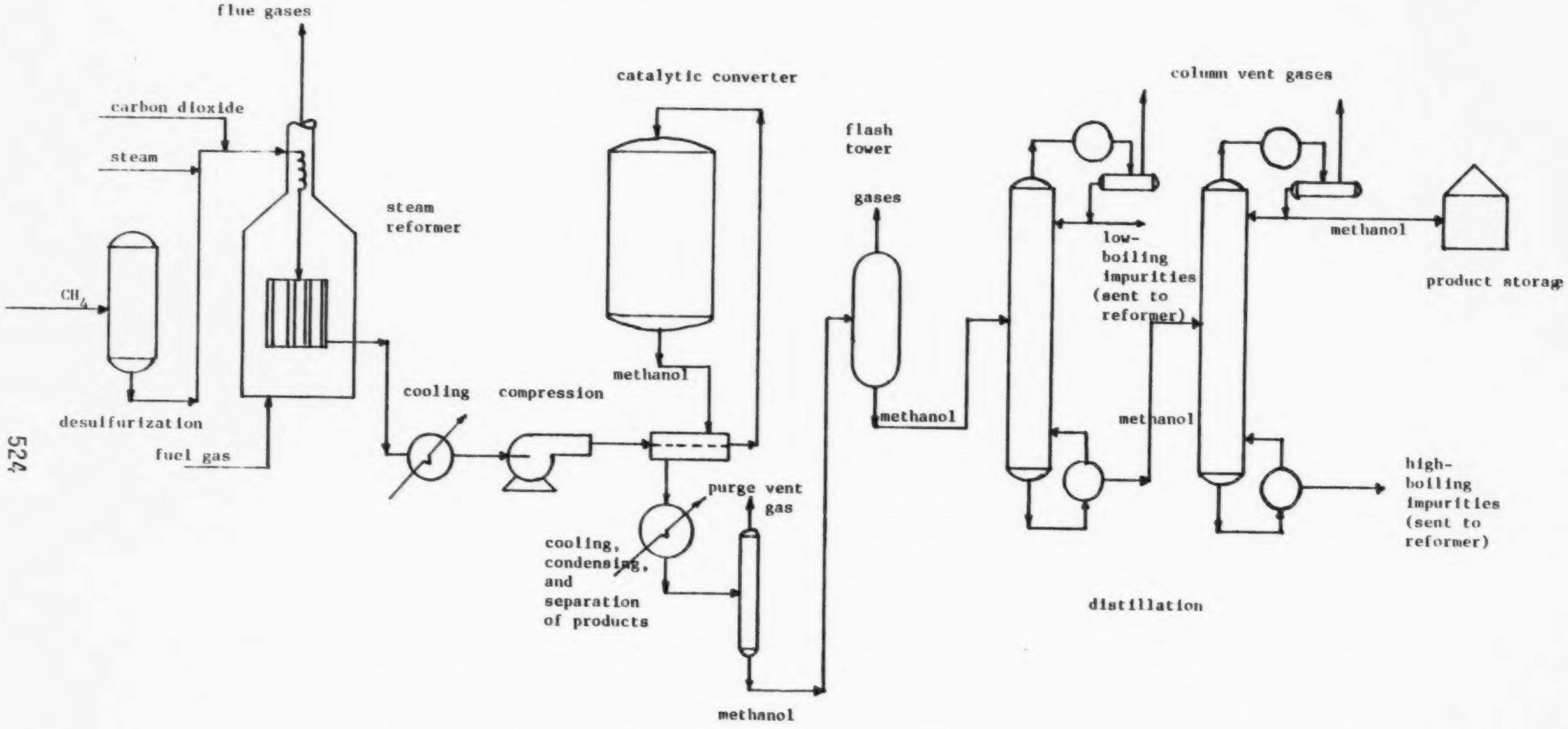
[a] Source: SRI 1981

These amounts are eighty percent of the capacities reported in SRI, 1981. A density of 49.3 lb/ft^3 (0.792 g/cm^3) was assumed. The ratio of production by high pressure to that of low pressure was obtained from White1980.

[b] High pressure process.

[c] Low pressure process.

Figure 23-1. Generalized Flow Diagram of a Reforming (steam) - Water Gas Process



a tubular reformer at 800°C over a promoted nickel-based catalyst. These reactions are endothermic. The high-pressure steam is pressurized from 16 to 21 atmospheres.

$$CH_4 + H_2O \xrightarrow[800^\circ C]{\text{catalyst}} CO + 3H_2 \tag{1}$$

$$CH_4 + 2H_2O \xrightarrow[800^\circ C]{\text{catalyst}} CO_2 + 4H_2 \tag{2}$$

Carbon dioxide is added to adjust the carbon to hydrogen ratio and also to push the reactions to make more carbon monoxide than carbon dioxide as in reaction (3).

$$H_2 + CO_2 \xrightarrow[800^\circ C]{\text{catalyst}} CO + H_2O \tag{3}$$

The hydrogen and carbon oxides are cooled from 800°C to 200°C in heat exchangers which recover heat by producing steam to be used as a reactant in reactions (1) and (2). They are converted to methanol in a catalytic converter operating at 200 to 300°C using a very active copper-based catalyst. These exothermic reactions proceed as follows:

$$2H_2 + CO \xrightarrow{\text{catalyst}} CH_3OH \tag{4}$$

$$3H_2 + CO_2 \longrightarrow CH_3OH + H_2O \tag{5}$$

The water from reaction (5) is an undesired by-product because it must be separated out and will be a contaminated waste stream. This is why the carbon dioxide is added to the reformer so that reactions (1) and (3) will make more carbon monoxide. The water from reaction (3) will be steam reformed, but the water from reaction (5) must be drawn off.

High-pressure and low-pressure processes refer to the pressure in the catalytic converter. High pressures range from 28 to 45 MPa (276-444 atm), and low pressures are from 5 to 10 MPa (49-99 atm). High-pressure processes use reciprocating pumps whereas low-pressure processes use centrifugal pumps. These processes also use different catalysts. High-pressure processes require high pressure in order to obtain adequate reaction rates, but the catalysts are less susceptible to sulfur poisoning. The very active copper-based catalyst used in low-pressure processes is easily poisoned by sulfur compounds. Therefore, the synthesis gas must contain less than 1.0 ppm sulfur, and preferably less than 0.1 ppm (USEPA 1980).

23.2 DESCRIPTION OF DISCHARGES

Releases from the reforming (steam) - water gas reaction occur as fugitive and particulate gaseous emissions, liquid wastes, and solid residues. The major sources of contamination are purge vent gases, regeneration gases, spent catalysts, and water from the purification section. Volatile organic compounds (VOCs) are emitted.

Fugitive gaseous emissions	- may occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains, and cooling towers.
Desulfurization of reactants	- release of hydrogen sulfide, methane, and steam will occur during regeneration of the desulfurization column. - spent catalysts will be landfilled.
Steam reforming of reactant	- emissions will occur, especially during regeneration. - spent catalysts will be landfilled.
Compression	- fugitive emissions will occur especially at compressor seals. - liquid wastes will result when the compressors are flushed and when the oil used to grease the compressors leaks out.
Catalytic converter	- emissions may occur; especially during regeneration. - spent catalysts will be landfilled.
Cooling and condensing	- a purge vent gas from the vapor-liquid separator is the largest process emission.

Distillation section	- vents on the distillation columns and flash tank will emit products and by-products.
	- a water waste stream will be removed and treated.

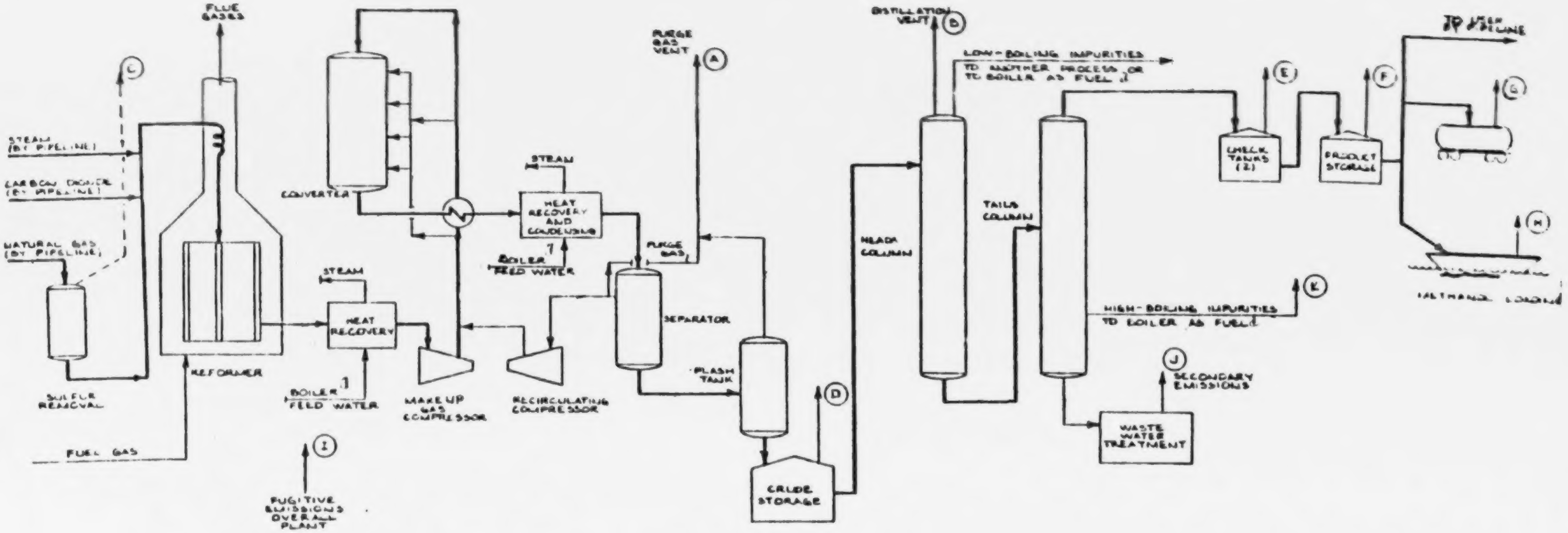
23.3 PRODUCTION PROCESS - METHANOL PRODUCTION

As stated earlier, almost all methanol produced in the United States is made from the reforming (steam) - water gas reaction. The process used most often is the low-pressure reaction of natural gas. Briefly, the process sequence is as follows. First, the methane is desulfurized by adsorption onto activated carbon. Then, high-pressured steam, methane, and carbon dioxide are reacted together in a tubular reformer to produce a synthesis gas consisting of carbon monoxide, carbon dioxide, and hydrogen. The synthesis gas is compressed to either a low pressure (5-10 MPa) or a high pressure (28-45 MPa) depending on whether the process is a low-pressure process or a high-pressure process. The synthesis gas passes to a catalytic converter where it is converted to methanol. After reaction, the methanol is cooled, condensed, and separated from the noncondensable by-products. Then, the methanol is sent to a flash tank and flashed to atmospheric pressure, thus releasing any dissolved non-condensable gases. The methanol contains high and low-boiling impurities. These impurities are separated from the methanol in distillation columns and reused as fuel for the reformer. The methanol product is checked to meet industry specifications and sent to storage tanks. Each of these process steps is discussed with emission points outlined and quantified when information was available. The model plant used by USEPA (1980) is a 450,000 Mg/yr plant operating 8760 hours per year. A detailed flow diagram is presented in Figure 23-2.

23.3.1 Desulfurization of Reactants

The natural gas entering contains a small amount of sulfur. Before it is reacted, the methane is desulfurized by adsorption of the sulfur onto activated carbon. The sulfur and some methane are removed by the activated carbon as the methane proceeds up the column. The carbon is the packing in

FIGURE 23-2 FLOW DIAGRAM FOR UNCONTROLLED MODEL PLANT FOR PRODUCTION OF METHANOL



Reproduced from best available copy.

SOURCE: White 1980

a Boiler refers to the reformer.

packed columns which are alternatively being used for desulfurization, regeneration, and purge. During regeneration, steam removes the sulfur deposits by reacting with the sulfur to produce hydrogen sulfide. The columns are purged when the activated carbon's life is completed. During regeneration and purging, intermittent waste streams are produced.

23.3.1.1 Emissions from Desulfurization of Reactants

Fugitive emissions will occur during normal operation of the desulfurization columns from valves, flanges, and leaks on the columns. An intermittent gaseous emission occurs twice per week during regeneration with steam (USEPA 1980). This emission contains hydrogen sulfide, methane, steam, and carbon fines. No VOCs will be emitted unless the incoming feed contains VOCs, which will be adsorbed by the activated carbon and desorbed during its steam regeneration (White 1980). The data in Table 23-2 shows the amount of sulfur removed for various methanol plants. The sulfur is removed to less than 1.0 ppm; therefore, the amount removed depends on the amount entering. No control devices were identified for the sulfur removal vent (White 1980). When the carbon life is completed, the whole bed of carbon is removed and replenished. Spent carbon is landfilled.

23.3.2 Steam Reforming of Natural Gas

Methane, high-pressure steam, and carbon dioxide are added to a tubular reformer which is fired with fuel gas to the reaction temperature of 800 to 850°C. The fuel gas usually consists of high and low-boiling impurities gathered from the distillation columns at the end of the process. The fuel gas is combusted in order to externally heat the tubes of the reformer. The combusted fuel gases exit from the top of the reformer as flue gas. The flue gas may contain uncombusted fuel gas.

The methane and steam undergo the endothermic reforming reaction within the tubes of the reformer which are packed with nickel-based catalysts. The exiting products are carbon monoxide, carbon dioxide, hydrogen, and unreacted steam and methane. Since the tubular reformer is packed with catalysts which are easily poisoned by sulfur compounds, it is occasionally shut down to regenerate or purge the catalysts. Downtime is

TABLE 23-2. EMISSIONS FROM A NATURAL GAS DESULFURIZER REGENERATION VENT

Plant	Properties of Plant's System		
Air Products			
Pensacola, Florida	Regeneration twice per week		
High Pressure Process	Flow 823 cfm		
of Natural Gas	Temperature 232°C		
	H_2S emissions	0.67 kg/hr	
		0.163 kkg/yr	
DuPont			
Beaumont, Texas	Regeneration	340 hr/yr	
High Pressure Process	Flow	375 kg/hr	127.5 kkg/yr
of Natural Gas	Total Emissions, kkg/yr		
	H_2S	0.13 kg/hr	
	CH_4	13.91 kg/hr	
	$C_2H_6, C_3H_8, C_4H_{10}$	0.51 kg/hr	
	H_2O	113.0 kg/hr	
	Temperature	100°C	
Tenneco			
Pasadena, Texas	Total Emissions, kkg/yr		
High Pressure Process	H_2O	526	
of Natural Gas	CH_4	118	
	Ethane	14.5	
	Propane	22	
	I-Butane	19	
	Temperature	216°C	

Source: White 1980. Vol. 9, Report 2, pp. D-2 to D-7.

estimated to be 5 to 15% of the operational time. The catalysts are regenerated with steam and purged when the catalyst's life is completed.

The exiting products are cooled from 800°C to 200°C in a heat recovery system which produces steam in heat exchangers with the excess heat. The cooled gases are then sent to the compression system.

23.3.2.1 Emissions from the Steam Reforming of Natural Gas

VOCs will be emitted in the flue gases exiting from the reformer because some of the fuel gas will not be completely combusted. The flue gases will be composed mainly of the combustion products, carbon dioxide, and water. Using the emission factors in AP-42 for distillate oil combustion, White (1980) has calculated that a minor emission of 0.000060 g of VOC/kg of methanol will be emitted.

No data were found for regeneration and purge of the reformer. It is assumed that when the catalyst life is completed, the spent catalyst will be landfilled and that the regenerating gases will contain methane, carbon monoxide, and carbon dioxide.

Emissions are expected in the heat recovery system; however, since the steam that is created is circulated to the reformer, it does not matter if it is contaminated with reactants or products. Fugutive emissions from leaks are expected.

23.3.3 Compression

In the compression step, the synthesis gas, both makeup gas and recycle gas, is compressed before it proceeds to the catalytic converter. There are two compressors: a make-up gas compressor and a recirculating compressor. If it is a high-pressure process, a pressure of 28 to 45 MPa will be obtained by using reciprocating compressors. On the other hand, if it is a low-pressure process, the synthesized gas will be pressurized to 5 to 10 MPa using centrifugal compressors (White 1980).

23.3.3.1 Emissions from Compressions

Fugitive emissions will occur from compression, especially at the compressor seals. Liquid wastes will result when the compressors are flushed. Also, the oil used to grease the compressors may leak out.

23.3.4 Synthesis of Methanol in a Catalytic Converter

The cooled, compressed makeup and recycled synthesis gases are mixed and preheated to the reaction temperature by heat exchange with the product gas leaving the converter. The preheated gas enters the converter where it is converted to methanol. The converter is a pressure vessel containing a single bed of a stable, copper-based methanol synthesis catalyst. It is operating in the pressure range of 5 to 10 MPa (49 to 99 atm) at 200 to 300°C. Cold synthesis gas is injected into the converter to maintain a constant temperature since the reaction is exothermic. The methanol product gas exits from the converter and is cooled through heat exchange with the incoming synthesis gas. The catalytic bed is regenerated or purged during process downtime as are the reformer catalysts.

23.3.4.1 Emissions from Synthesis of Methanol in a Catalytic Converter

No emissions data were found for the catalytic converter. Since the converter is a pressurized vessel, fugitive emissions are expected to be minor. If the leak were major, the drop in pressure would be detected and the leak rapidly fixed. Minor leaks within the heat exchangers are not considered serious since both gases flowing are products and reactants.

23.3.5 Cooling and Condensing

The crude methanol product is further cooled in a heat exchanger where the sensible heat is recovered by heating reactant steam. The methanol stream is then passed through a condenser where the methanol is condensed. The unreacted synthesis gas and the condensed methanol proceed to a vapor-liquid separator where the crude methanol is removed from the unreacted gas. The crude methanol is sent to a flash tank. Most of the unreacted gas is recycled to the converter via the recirculating compressor. Some of the unreacted gas is purged through the purge vent on the separator. An estimated composition of the purge vent gas is shown in Table 23-3.

23.3.5.1 Emissions from Cooling and Condensing

The purge vent gas on the separator is the largest process emission (White 1980). This gas may be recycled to the reformer and used as fuel, flared, or directly released to the atmosphere. The water and steam may become contaminated through leaks in the condenser and heat exchangers. Since these are reactant water being evaporated and then reactant steam being preheated before reaching the reformer, a small amount of contamination will not matter. Reforming gas processes utilize their excess energy by heating reactants while cooling products in their heat exchangers. They do not use cooling water, which eliminates cooling water contamination problems.

23.3.6 Distillation for Product Purification

The crude methanol product contains impurities, such as dissolved gases, low-boiling impurities, and high-boiling impurities, which are removed in the distillation section. Minimal carry-over of metal catalyst is expected (USEPA 1974). First, the crude methanol is sent to a flash tank where it is flashed to atmospheric pressure, thus releasing the dissolved gases. These dissolved gases are purged with the purge gas from the separator.

The degassed methanol then proceeds to the heads distillation column where the low-boiling impurities are separated from the crude methanol. The low-boiling impurities are mostly dimethyl ether and methyl formate and are removed as the overhead product and recycled to the reformer to be used as fuel. The crude methanol exits as the bottoms product and proceeds to the tails column.

The tails column or refining column separates the high-boiling impurities, such as higher alcohols and water, from the methanol. The methanol product is removed as the overhead product which is then checked to make sure it meets industry specifications and sent to storage tanks.

TABLE 23-3 ESTIMATED COMPOSITION OF PURGE VENT GAS FROM MODEL PLANT[a]

Component	Composition wt%	Emission Ratio kg/kkg product
Methanol	0.8	1.1
Methane	64.8	88.1
Hydrogen	15.1	20.6
Carbon monoxide	11.1	15.1
Nitrogen[b]	4.9	6.7
Carbon dioxide	3.1	4.2
Water	0.2	0.2
Total	100	136

[a] Model plant produces 450,000 kkg/yr of methanol.

[b] Sometimes nitrogen and argon enter in the natural gas feed.

Source: White 1980. Volume 9, Report 2, p. IV-4.

The higher alcohols are removed through a sidearm near the bottom of the tails column and sent to the reformer to be used as fuel. Water is removed as the bottoms product and sent to a wastewater treatment section.

23.3.6.1 Emissions from Distillation for Product Purification

The purge gas from the flash tank is added to the purge gas from the separator and either recycled to the reformer to be used as fuel, flared, or released directly to the atmosphere. Fugitive emissions may occur from the flash tank.

The distillation columns have pressure-relief vents which continuously release non-condensable gases that are dissolved in the crude methanol. Table 23-4 shows the estimated composition of the gases emitted from these vents (White 1980). These gases are usually flared or used as fuel gas in the reformer.

The water as the bottoms product of the tails column contains 100 to 300 ppm organics, mostly methanol (White 1980). This is the only wastewater from the process, except for vessel washdowns, and it is sent to the wastewater treatment system. There are no wastewater differences between high-pressure and low-pressure processes (USEPA 1974). Hedley (1975) estimates for a 907 kkg/day high-pressure process that the by-products per kkg of methanol are: 19.3 kg of mixed alcohols (methanol and higher alcohols) and 20.4 kg of dimethyl ether and methyl formate. He also estimates that the wastewater stream amounts to 100 to 500 gallons of water/ton of product which contains some oil, methanol, and higher boiling organics to the extent of several hundred mg/l.

23.4 SUMMARY OF EMISSION DATA

A summary of the emission data found on the production of methanol by the reforming (steam) - water gas reaction is tabulated in Table 23-5. The areas of environmental concern are the vents on the separator, distillation columns, and desulfurization column; the wastes exiting with the regeneration gases of the desulfurization column, the reformer, and the catalytic converter; and the wastewater released as the bottoms product

TABLE 23-4. ESTIMATED COMPOSITION OF THE DISTILLATION VENT GAS FROM MODEL PLANT[a]

Component	Composition Wt%
Methanol	29.0
Dimethyl ether & methyl formate[b]	12.1
Total VOC	41.1
Carbon dioxide	58.6
Water	0.3
Total	100

[a] Model plant produces 450,000 kkg/yr of methanol.

[b] It is estimated that 5% of the dimethyl ether and methyl formate are not condensed.

Source: White 1980. Volume 9, Report 2, p. IV-5.

TABLE 23-5. ESTIMATED RELEASE FROM METHANOL PRODUCTION BY STEAM REFORMING-WATER GAS PROCESS OF NATURAL GAS

					Uncontrolled Emissions			Controlled Emissions	
Pollutant	Location	Source	Type of Release +	Receiving Medium	Quantity kg/kkg product	Rate kg/hr	Form	Control Technology	Quantity kg/kkg
VOCs[a]	purge gas vent (A)	by-products	r	air	1.1	56.5	gas	used as fuel	0.019
	distillation vent (B)	by-products	r	air	0.4	20.5	gas	flare	0.008
	sulfur removal (C)	contaminants	r	air	b	b	gas	NA	NA
	storage vents								
	crude methanol (D)	product	r	air	0.0097	0.50	gas	internal-floating	0.0014
	check tanks (E)	product	r	air	0.08	4.1	gas	roof tanks	0.012
	product (F)	product	r	air	0.365	18.8	gas		0.055
	handling								
	loading tank cars (G)	product	r	air	0.0486	2.49	gas	aqueous scrubber	0.000486
	loading barges (H)	product	r	air	0.0971	4.99	gas	aqueous scrubber	0.000971
	fugitive (I)	products	r	air	0.578	29.7	gas	detection & correction of major leaks	0.116
	secondary								
	wastewater treatment (J)	by-products	r	air	0.00044	0.023	gas	NA	NA
	waste organic as fuel (K)	by-products	r	air	0.000060	0.0031	gas	NA	NA
	TOTAL			air	2.68	138	gas		
COD	raw waste load in water 59 gal/1000 lb of methanol[c]	by-products	r	water	0.16	32 mg/l	liquid	NA	NA
BOD_5		by-products	r	water	0.059	119 mg/l	liquid	NA	NA
TOC		by-products	r	water	0.053	107 mg/l	liquid	NA	NA
Mixed Alcohols	wastewater from refining column[d]	by-products	r	water	19.3	730	liquid	NA	NA
Dimethylether		by-products	r	water	20.4	771	liquid	NA	NA

Source: White 1980. Vol. 9, Report 2, pp. IV-3 and V-2.

+ r means routine

a Basis: 450,000 kkg/yr production of methanol

b No VOCs are released unless VOCs are present in the incoming feed.

c Source: USEPA 1974.

d Source: Hedley 1975. Basis: 907 kkg/day high-pressure process.

from the methanol purification section. These wastes will vary depending on the purity of the incoming feed as demonstrated in Table 23-6. These wastes will also vary depending on the maintenance, age of equipment, and operating conditions. The model plant was very energy efficient as are most reforming (steam) - water gas processes (White 1980).

TABLE 23-6. COMPARISON OF RAW WASTE LOADS USING DIFFERENT FEEDSTOCKS

Feedstock	Natural Gas	Acetylene Off-gases
Flow	492 liters/kkg	352 liter/kkg
COD	320 mg/l 0.16 kg/kkg	4930 mg/l 1.74 kg/kkg
BOD_5	119 mg/l 0.059 kg/kkg	2620 mg/l 0.92 kg/kkg
TOC	107 mg/l 0.053 kg/kkg	583 mg/l 0.21 kg/kkg

Source: USEPA 1974.

REFERENCES

Hedley, W.H., S.M. Mehta, C.M. Moscowitz, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Co.

Herrick, E.C., J.A. King, R.P. Oullette. 1979. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

SRI International. 1981. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

USEPA. 1974. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemical Manufacturing. Point Source Category. Washington, D.C.

White. 1980. U.S. Environmental Protection Agency. Organic Chemical Manufacturing, Volume 9: Selected Processes. Research Triangle Park, NC: Office of Air Quality. EPA-450/3-80-028d.

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SECTION 24

SULFONATION AND SULFATION

24.0 INTRODUCTION

Sulfonation is the process by which the sulfonic acid group ($\cdot SO_2OH$), the corresponding salt ($\cdot SO_2O^-$), or the sulfonyl halide ($\cdot SO_2OX$) is attached to a carbon or a nitrogen atom. Sulfonation is also used to indicate treatment of any organic compound with sulfuric acid, regardless of the nature of the products formed. Sulfation involves the placement of an $\cdot OSO_2OH$ group on carbon when sulfating an alkene or of an $\cdot SO_2OH$ group on oxygen when sulfating an alcohol or a phenol.

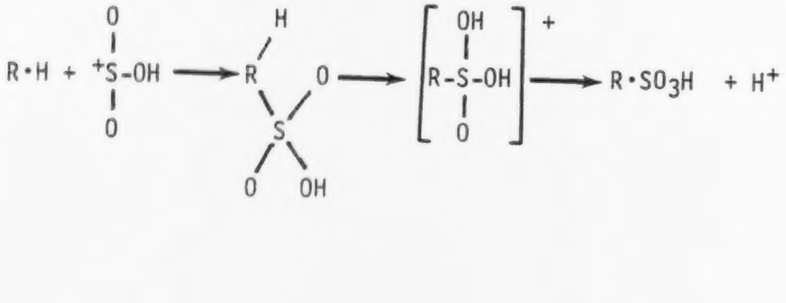
The sulfonation and sulfation processes are similar. Each process includes a reactor vessel which is usually agitated, a neutralization tank, and a method of purification and separation. Figure 24-1 is a typical process diagram. The principal organic chemicals manufactured by sulfonation and sulfation are listed on Tables 24-1 and 24-2.

24.1 GENERAL CHEMISTRY

Sulfonation renders compounds more soluble in water or provides a route to other substituents. Direct sulfonation is achieved with (1) strong sulfuric acid, (2) oleum (sulfuric acid plus sulfur trioxide), (3) sulfur trioxide in organic solvent or as a complex, or (4) chlorosulfonic acid. The reaction may be expressed as follows:

$$R\cdot H + H_2SO_4 \longrightarrow R\cdot SO_2OH + H_2O$$

The actual sulfonating agent is believed to be the cation, $^+SO_3H$.



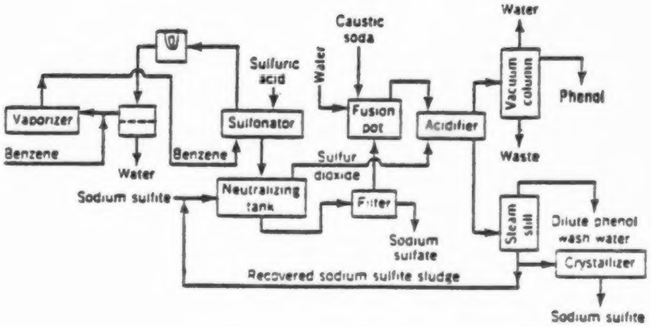


FIGURE 24.1 FLOW CHART OF A TYPICAL SULFONATION PROCESS - THE MANUFACTURE OF PHENOL FROM BENZENE

TABLE 24-1. SULFONATION PRODUCTS AND THEIR PRODUCTION IN 1979

Product	Amount kkg	Feedstock	Other Required Processes
Alkylbenzene sulfonates	295,025	Alkylbenzenes, sulfur trioxide	Hydrolysis
m-Aminophenol	NA	Nitrobenzene	Hydrogenation Hydrolysis
Methyl methacrylate monomer	418,893	Acetone Hydrogen cyanide Methanol	Esterification Hydrocyanation Hydrolysis
2-Naphthol	NA	Naphthalene Caustic soda	
Phenol	36,263	Benzene Caustic soda Sulfuric acid	

Source: Herrick, et al. 1979; Synthetic Organic Chemicals 1980.

Note: Sulfonation is not always the major method of production of these chemicals.

TABLE 24-2. SULFATION PRODUCTS AND THEIR PRODUCTION IN 1979

Product	Amount kkg	Feedstock	Other Required Processes
Alcohol, mixed linear sulfated -,ammonium salt -,sodium salt -,triethanolamine salt -,unspecified	110,865	Fatty alcohols, sulfur trioxide	Hydrolysis
Sec-Butyl alcohol	NA*	Butylene	Hydrolysis
Ethoxylsulfates	NA	Ethoxylates, sulfur trioxide	None
Isopropyl alcohol	855,169	Propylene	Hydrolysis

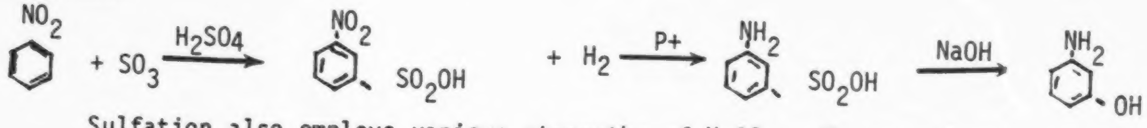
Source: Herrick, et al. 1979; Synthetic Organic Chemicals 1980.

Note: Sulfation is not always the major method of production of these chemicals.

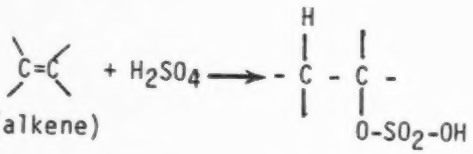
*-Estimated at 250,000 kkg in 1976, Kirk-Othmer.

Depending on what product is being sulfonated, there is a critical concentration of sulfuric acid below which sulfonation ceases. For example when producing phenol from benzene, if the concentration of sulfuric acid drops below 78 percent, the sulfonating action ceases.

The sulfonation of nitrobenzene to form m-Aminophenol occurs as follows:



Sulfation also employs various strengths of H_2SO_4. The reactions can be generalized as follows:



(alkene)

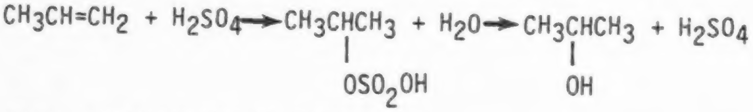
$R \cdot OH + H_2SO_4 \longrightarrow R \cdot O\text{-}SO_2OH + H_2O$

(alcohol)

$Ar\text{-}OH + H_2SO_4 \longrightarrow Ar\text{-}O\text{-}SO_2OH + H_2O$

(phenol)

The sulfation of propylene to form isopropyl alcohol occurs as follows:



$$CH_3CH{=}CH_2 + H_2SO_4 \rightarrow \underset{\displaystyle OSO_2OH}{CH_3\underset{|}{C}HCH_3} + H_2O \rightarrow \underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3} + H_2SO_4$$

24.2 DESCRIPTION OF DISCHARGES

Releases from a typical sulfonation or sulfation process occur in wastewater, as vent gases, and as fugitive gaseous emissions.

Fugitive: occur from valves, flanges, pump seals, compressor seals, pressure relief valves, drains and cooling towers, and storage tanks.

Sulfonation/sulfation section: neutralization crystals.

Product Purification: vent gases from columns and wastewater from columns.

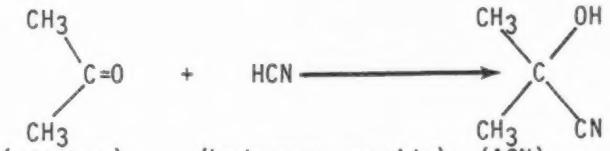
24.3 PRODUCTION OF METHYL METHACRYLATE BY SULFONATION AND RESULTING EMISSIONS

All methyl methacrylate (MMA) in the United States is manufactured from acetone and hydrogen cyanide. Acetone cyanohydrin (ACN) is produced from acetone and hydrogen cyanide. Then methyl methacrylate is formed from the acetone cyanohydrin.

The following discussion of the production of methyl methacrylate and its emissions is divided into six subsections: (1) acetone cyanohydrin reaction and emissions, (2) neutralization and filtration and emissions, (3) purification and recovery columns and emissions, (4) methacrylamide sulfate reaction and vapor-liquid separator and emissions, (5) methyl methacrylate reaction and liquid-liquid separation, and (6) purification and recovery columns and emissions. The discussion is based on information from White 1980 and Gruber 1975.

24.3.1 Acetone Cyanohydrin Reaction

The reaction to manufacture ACN is reported as:

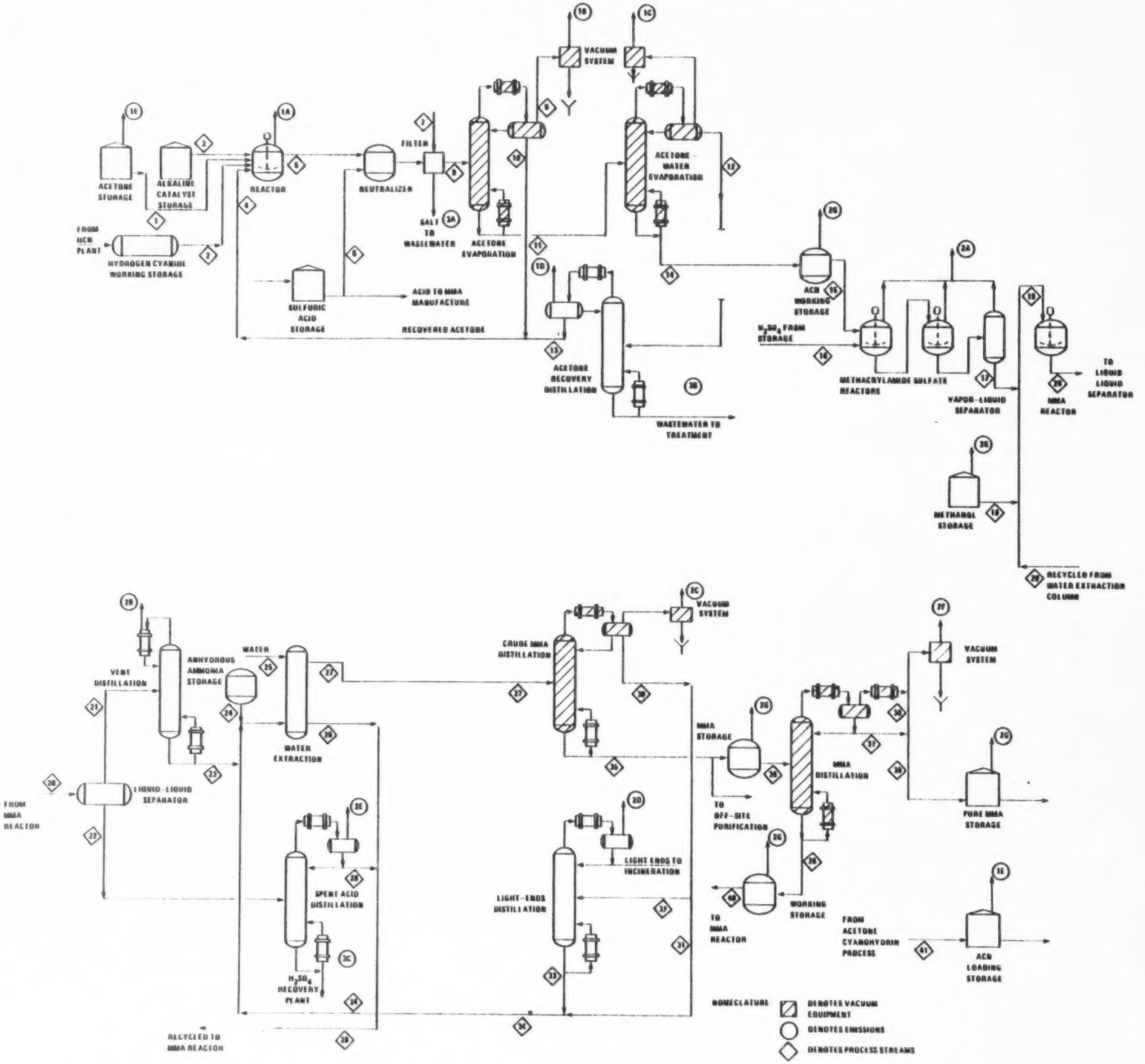


(acetone) (hydrogen cyanide) (ACN)

Figure 24-2 is a detailed flow diagram of the process.

Acetone is stored in tanks before being fed to the process (Stream 1). Hydrogen cyanide (Stream 2), usually produced elsewhere at the same plant, may be stored temporarily before being fed to the reactor. The catalyst (Stream 3), an alkali such as sodium hydroxide or other bases, is also stored. Acetone recovered later in the process (Stream 4) is combined with the other reactants in the agitated reactor to form acetone cyanohydrin. The liquid-phase acetone cyanohydrin reaction is carried out at less than 40°C, with yields above 90% usually attained. Acetone cyanohydrin readily decomposes at higher temperatures.

FIGURE 24-2 FLOW DIAGRAM FOR THE MANUFACTURE OF METHYL METHACRYLATE



24.3.1.1 Emissions

There is a low-rate reactor off-gas (Stream 1A) (White 1980). The emission is composed of acetone and hydrogen cyanide and is currently being controlled by condensers or by being sent to a flare.

24.3.2 Neutralization and Filtration

The sodium hydroxide in the product stream (Stream 5) is neutralized with sulfuric acid (Stream 6) to stabilize the ACN. The solid salts formed are removed by filtration and backwashed with water (Stream 7).

24.3.2.1 Emissions

The backwash water results in a sulfate salt crystal which is removed by filtration. The sulfate salt, after being washed, is sent to land disposal.

24.3.3 Purification and Recovery Columns

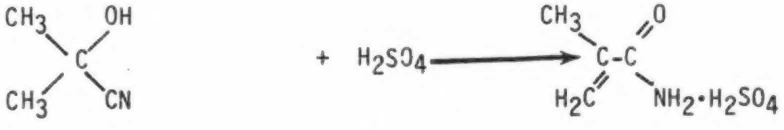
The filtered crude reaction product (Stream 8) enters a vacuum evaporation system for acetone removal (Stream 10), and the acetone cyanohydrin bottoms (Stream 11) is fed to a second evaporator. The second evaporator removes water and trace acetone (Stream 12), leaving acetone cyanohydrin product (Stream 14). The distillate from the second evaporator (Stream 12) is further distilled in an acetone recovery column, and the recovered acetone (Stream 13) is recycled (Stream 4) to the reactor.

24.3.3.1 Emissions

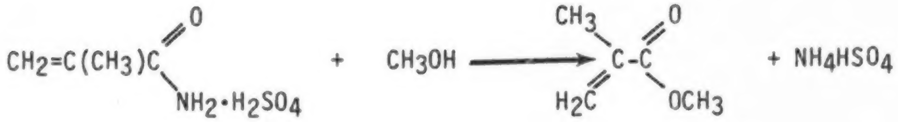
There are vent gas streams from the product distillation columns and acetone recovery column. To reduce acetone loss from these streams, condensers are used. These condensers are not considered to be emission control devices unless they operate beyond economic optimum. One plant passes these vent gases through an incinerator. Also, there is wastewater from the acetone recovery distillation column, which is sent to treatment.

24.3.4 Methacrylamide Sulfate Reaction and Vapor-liquid Separator

The reaction of ACN to MMA involves the formation of methacrylamide sulfate from ACN. The methacrylamide sulfate is then reacted with methanol to form MMA. The reactions describing this process are as follows:



(acetone cyanohydrin) (sulfuric acid) (methacrylamide sulfate)



(methacrylamide sulfate) (methanol) (MMA) (ammonium bisulfate)

Figure 24-2 is a typical process flow diagram for the manufacture of MMA from ACN. The ACN (Stream 15) is stored until it is to be fed to the reactor. Sulfuric acid (Stream 16) is also fed to the reactor, forming methacrylamide sulfate. Two reactors are operated at 130°C, and the ACN-sulfuric acid reaction is highly exothermic (60 kcal/g-mole). Vapors are removed from the product stream in a vapor-liquid separator.

24.3.4.1 Emissions

The emissions (Stream 2A) are the vapors from the vapor-liquid separator and the vapors from the reactor vents. The emissions are composed primarily of sulfur dioxide, carbon monoxide, and other reaction by-products. There are also traces of ACN and acetone. Currently the emissions are sent to a flare or are not being controlled.

24.3.5 Methyl Methacrylate Reaction and Liquid-liquid Separation

From the vapor-liquid separator, the product (Stream 17) is fed to the MMA reactor with fresh methanol (Stream 18) and recovered methanol (Stream 29). The reactor effluent is a two-phase liquid mixture (Stream 20), which is fed to a liquid-liquid separator.

24.3.6 Vent Distillation and Water Extraction Columns

The light phase from the liquid-liquid separator (Stream 21) is distilled in a vent distillation column designed to remove dissolved carbon monoxide (Stream 2B). Then the light phase (Stream 23) is neutralized with anhydrous ammonia (Stream 24) and fed to a water extraction column. MMA and methacrylic acid recovered later in the process (Stream 34) are also fed to the water extraction column. The extract (Stream 26) from the water extraction column contains water, ammonia bisulfate, methanol, and other water-soluble compounds; the raffinate (Stream 27) contains the MMA and similar organics.

24.3.6.1 Emissions

The bottoms from the vent distillation column in processes without a liquid-liquid separator constitute a hazardous waste stream and are sent to land disposal. They contain polymers and hydroquinone.

24.3.7 Spent Acid Distillation Column

The heavy phase from the liquid-liquid separator (Stream 22) is distilled in a spent acid distillation column, where light organics such as methanol are removed (Stream 28). The light organics (Stream 28) are combined with the extract (Stream 26) from the extraction column and recycled to the MMA reactor (Stream 29). Bottoms from the spent acid distillation column are routed to the sulfuric acid recovery plant or to ammonia sulfate production.

24.3.7.1 Emissions

The bottoms (Stream 3C) from the spent acid distillation column contains ammonium acid sulfate, residual sulfuric acid, and organics. They constitute a hazardous process waste which is either sent to a recovery unit or discharged to a sewer.

24.3.8 Crude MMA Distillation, Light Ends Distillation and MMA Distillation Columns

The raffinate (Stream 27) from the water extraction column is distilled in a vacuum distillation column, where the light ends (Stream 30) are removed. This stream is split, with some of it recycled (Stream 31) to the water extraction column and some of it (Stream 32) further distilled to remove the light ends to prevent their buildup in the system. The bottoms (Stream 33) from the light-ends distillation column are recycled to the water extraction column (Stream 34).

Crude MMA leaves the crude MMA distillation column as the bottoms stream (Stream 35) which can be distilled at the production location or can be transported for further purification at other sites. The distillation proceeds under vacuum, and the bottoms (Stream 40) are recycled to the MMA process. The distillate is pure MMA and is stored for shipping and/or processing. ACN that is marketed (Stream 41) is also stored in preparation for shipping.

24.3.8.1 Emissions

The light ends from the crude MMA column go to the plant industrial outfall. They contain hazardous components whose removal via land based treatment techniques would be required by the Federal Water Pollution Control Act Amendments. The hazardous components would be destined for land disposal.

24.3.9 Purification and Recovery Columns Emissions

The gases from the vent distillation column (Stream 2B), the crude MMA distillation column (Stream 2C), the light ends distillation column (Stream 2D), the spent acid distillation column (Stream 2E), and the product MMA distillation column are composed of: noncondensables that are dissolved in the feed to the columns; VOC that are not condensed; and, for columns operated under vacuum, air that leaks into the column and is recovered by a vacuum, jet system. The emissions are primarily controlled by condensers, which are usually included as part of the processing condensers. In one case, some of the vent emissions are combined and sent to a flare, which achieves 99+% VOC reduction.

24.3.10 Secondary Emissions

The secondary emissions related to MMA production are from organic wastes routed to an incinerator or acid recovery unit, from intermittent aqueous wastes that are sent to a sewer, and from spent acid and aqueous wastes that are sent to sulfuric acid recovery.

The organic wastes generated are polymeric material formed during MMA production, acid recovery, or incineration. The polymer goes to landfill or incineration.

The spent acid has been reported to contain methyl methacrylate, methacrylic acid, methyl formate, methanol, and acetone. Emissions from sulfuric acid recovery can be a significant fraction of the controlled VOC emissions levels.

24.4 SUMMARY OF EMISSIONS DATA

Table 24-3 summarizes the emissions from the methyl methacrylate manufacturing process. Figure 24-2 shows the stream numbers on the flow diagram.

The major method of production of the chemicals listed in Tables 24-1 and 24-2 is not always sulfonation or sulfation. Therefore, emissions data are not always accessible. No information was available on the emissions from any other sulfonation or sulfation process.

TABLE 24-3. ESTIMATED RELEASES FOR METHYL METHACRYLATE PRODUCTION

					Uncontrolled Emissions			Controlled Emissions		
Pollutant	Location	Source	Type of Release	Receiving Medium	quantity kg/kkg product	rate kg/hr	Form	control technology	quantity kg/kkg product	Stream No.
Acetone hydrogen cyanide	acetone cyanohydrin feed tanks	feed	r	air	29.5[2] 3.15[2]	NA NA	gas gas	none none	- -	1E
Acetone & hydrogen cyanide	acetone cyanohydrin reactor off-gas	feed	r	air	0.039[1]	NA	gas	condenser	0.004	1A
Sulfate salt crystal	filtration of crude acetone cyanohydrin	by-product	r	land	100[1]	NA	solid	washed	NA	3A
NA	vent gases from acetone cyanohydrin distillation and recovery columns	NA	r	air	0.004-1.17[1]	NA	gas	none	0.004-1.17	1B, 1C, 1D
NA	wastewater from acetone recovery	NA	r	water	NA	NA	NA	treatment	NA	3B
Sulfur dioxide, carbon monoxide, and other reaction by-products, traces ACN, and acetone	methacrylamide sulfate reactors*	by-product, product, feed	r	air	NA	NA	gas	flare or nothing	NA	2A
55.3% Ammonium acid sulfate 42.2% Residual sulfuric acid 0.5% Methanol 0.3% Polymers 0.9% Ammonium methacrylate 0.04% Ammonium acetate 0.9% Ammonium cyanide	bottoms sulfuric acid recovery column	by-product, feed	r	water	2278[2]	NA	liquid	recovery unit	NA	3C

TABLE 24-3. ESTIMATED RELEASES FOR METHYL METHACRYLATE PRODUCTION (CONTINUED)

Pollutant	Location	Source	Type of Release	Receiving Medium	Uncontrolled Emissions: Quantity kg/kkg product	Uncontrolled Emissions: Rate kg/hr	Form	Controlled Emissions: Control Technology	Controlled Emissions: Quantity kg/kkg product	Stream No.
87% Polymers 13% Hydroquinone	bottoms vent distillation	by-product	r	land	76[2]	NA	liquid	none	-	for plant without liquid-liquid separator
92% Acetone 1% Hydroquinone 6% Methyl methacrylate 1% Hydrogen cyanide	light end from crude MMA column	by-product	r	land	29[2]	NA	liquid	NA	NA	"
Noncondensables in feed, uncondensed VOC, air leaks being removed	methyl methacrylate purification and recovery columns	by-product	r	air	21[1] NA NA 6.62[1] 4.74[1] 2.65[1]	NA NA NA NA NA NA	gas	flare NA NA none none condenser	0.21[1] 0.007[1] 19[1] 6.62[1] 4.74[1] 0.087[1]	2A,2B,2C, 2D,2E 2F 2A,2E 2B,2C,2D 2F

Sources:

[1] White 1980.
[2] Gruber 1975.

+Denotes that a release is routine (r) or accidental (a).

*The sulfonation process starts at this point.

REFERENCES

Considine, D. 1974. Chemical and Process Technology Encyclopedia. New York: McGraw-Hill Book Company.

Faith, W. L., D. B. Keyes, and R. L. Clark. 1965. Industrial Chemicals, 3rd ed. New York: John Wiley and Sons, Inc.

Gruber, G. I. TRW Systems Group. 1975. Assessment of Industrial Hazardous Waste Practices, Organic Chemicals, Pesticides, and Explosives Industries. U.S. Environmental Protection Agency. Office of Solid Waste. Washington, D.C. EPA/530/SW-118C.

Hedley, W. H., S. M. Mehta, C. M. Moscowitg, et al. 1975. Potential Pollutants from Petrochemical Processes. Westport, Connecticut: Technomic Publishing Company, Inc.

Herrick, E. C., J. A. King, R. P. Ouellette and P. N. Cheremisinoff. 1979a. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Michigan: Ann Arbor Science Publishers, Inc.

Hydrocarbon Processing. 1973. 1973 Petrochemical Handbook Issue. Houston, Texas: Gulf Publishing Company.

Kent, James A. 1974. Riegel's Handbook of Industrial Chemistry. New York: Van Nostrand Reinhold Company.

Kirk-Othmer. 1979. Encyclopedia of Chemical Technology, 3rd ed. Volumes 2 and 4. New York: John Wiley and Sons, Inc.

Monsan, Richard S., and John C. Sholton. 1974. Fundamentals of Organic Chemistry. New York: McGraw-Hill Book Company.

Parsons, T. B., C. M. Thompson, and G. E. Wilkins. 1977. Industrial Profiles for Environmental Use. Chapter 5. Basic Petrochemicals Industry. Radian Corporation. For: Office of Research and Development, Industrial Environmental Research Laboratory. Research Triangle Park, North Carolina: U. S. Environmental Protection Agency. EPA-600/2-77-023e.

Shreve, R. N. 1967. Chemical Process Industries, 3rd ed. New York, New York: McGraw Hill Book Company.

Solomons, T. W. Graham. 1978. Organic Chemistry, revised printing. New York: John Wiley and Sons.

REFERENCES
(continued)

SRI International. 1981 Directory of Chemical Producers - United States of America. Menlo Park, California.

U.S. EPA. 1981. Supplement 12 for Compilation of Air Pollutant Emission Factors. Research Triangle Park, N.C.: U.S. EPA Office of Air and Water Management and Office of Air Quality Planning and Standards.

U.S. ITC. 1979. United States Production and Sales. Synthetic Organic Chemicals. U.S. Department of Commerce.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volume 10. For Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028e.

REFERENCES EVALUATED BUT NOT USED

The following computerized data files were consulted:

Chemical Abstract Search
Patent Claims/Class
Compendex (Engineering Index)

APPENDIX B

STANDARD FORMAT FOR THE ENVIRONMENTAL RELEASE REPORTS

Table B-1 STANDARDIZED FORMAT FOR THE ENVIRONMENTAL RELEASE REPORTS

Subsection	Title	Comments
0	Introduction	Reviews the process briefly (1/2 paragraphs) including the major unit operations. Mentions if the process is catalytic/non-catalytic. Includes a flow diagram of a typical process. Lists principal chemicals (including latest data on production levels by the mentioned process) and principal feedstocks used.
1	General Chemistry	Describes the principal reactions that take place.
2	Description of Discharge	Describes in words the principal air, water, and solid waste emissions (routine and fugitive).
3	Production Process	Provides a detailed manufacturing process description for that chemical with the highest production volume.
4	Summary of Emissions Data	Includes a process flow diagram indicating location of emissions points. Includes a quantitative table of emissions. Separate flow diagrams and a table of emissions are prepared for major manufacturing processes.
5	Bibliography	Each section has its own bibliography.

APPENDIX C

A PORTFOLIO OF SOCMI MULTIMEDIA EMISSION CHARACTERISTICS - BY UNIT PROCESS AND BY UNIT OPERATIONS

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C-1 Estimated Total VOC Emissions from Process, Fugitive, Storage, and Secondary Sources for Major Unit Processes

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C-3 Categorization of Wastewaters Generated by 23 Unit Processes

C-4 Major Raw Waste Loads of Pollutants Based on Process Wastewater

C-5 Treated Wastewater Effluents for Polymerization Processes

C-6 Releases from Heating and Cooling Equipment in the SOCMI

C-7 Releases from Absorption, Distillation, and Stripper Columns

C-8 Releases from Some Unit Operations in the SOCMI

C-9 Possible Reactor Releases

C-10 Nationwide Unit Operations Emission Characteristics in the SOCMI

C-11 SOCMI Unit Operations Waste Water Effluents

C-12 SOCMI Unit Operations Which Generate Solid Wastes

C-13 Equations Used for Calculating Air Emissions for Inert-Carrier Gas Method (Using Chlorination Reactions As An Example) $a R + b Cl_2 \longrightarrow cRCl + dHCl$

C-14 Equations Used for Calculating Air Emissions For Reaction Using Air As Its Source of Oxygen[1]

TABLE C-1. ESTIMATED TOTAL VOC EMISSIONS FROM PROCESS, FUGITIVE, AND STORAGE AND SECONDARY SOURCES FOR MAJOR UNIT PROCESSES BASED ON EARLY ITE RANKING STUDIES

Unit Process	1982 Estimated Production ($\overline{M}$* lb/yr)	Average Release Factor lb/lb	1982 Estimated Total VOC Emissions ($\overline{M}$ lb/yr)
Oxidation	37,300	0.014	528
Ammoxidation	3,420	0.088	301
Esterification	7,700	0.024	182
Chlorination	16,100	0.011	175
Pyrolysis (chlorinolysis)	56,100	0.003	173
Dehydrochlorination	9,500	0.010	91
Oxychlorination	6,030	0.012	72
Alkylation	14,400	0.004	59
Hydrolysis	1,900	0.029	56
Hydration	10,800	0.005	52
Hydrogenation	7,210	0.004	31
Hydrochlorination	2,020	0.011	22
Condensation	14,300	0.001	20
Dehydrogenation	10,900	0.001	13
Dehydration	12,200	0.001	10
Sulfonation	3,710	0.002	9
Nitration	2,380	0.003	8
Carbonylation	1,080	0.006	7
Phosgenation	1,630	0.004	7
Hydrofluorination	1,000	0.005	5
Amination by Ammonolysis	1,380	0.003	4
Hydrodealkylation	4,030	0.001	3
Addition esterification	290	0.007	2
Bromination	220	0.005	1

*Designates one million.

Source: White 1980.

TABLE C-2. CATEGORIZATION OF WASTEWATERS GENERATED FROM THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY

Subcategory	Title & Description
A	Continuous Non-Aqueous Processes: Contact between water and reactants is minimal. Water is not required as either reactant or diluent, and is not formed as a reaction product. The only water usage stems from periodic washes and catalyst hydration.
B	Continuous Vapor Phase Processes Where Contact Process Water is Used as Diluent, Quench, or Vent Gas Absorbent Process water is generated through the use of diluent steam, product quench, or vent gas absorption. Process reactions are all vapor-phase over solid catalysts. Most processes use a vent gas absorber, coupled with steam stripping of chemicals for purification and recycle of the absorber water. Non-contact water is also used.
C	Continuous Aqueous Liquid-Phase Reaction Systems Process reactions are liquid-phase, with the catalyst in the aqueous medium. Continuous regeneration of the catalyst requires extensive water usage, and substantial removal of spent catalysts and inorganic by-products may be required. Addition process water is involved in final purification and/or neutralization of products. Non-contact water is also used.
D	Batch and Semicontinuous Processes Many reactants are in the liquid-phase with aqueous catalyst systems. Requirements for very rapid processing cooling necessitates provisions for the direct addition of contact quench water or ice. Reactants and products are transferred from one piece of equipment to another by gravity flow, pumping or pressurization. Much of the materials handling is manual, and there is only limited use of automatic process control. Filter presses and centrifuges are commonly used for solid-liquid separations, and air or vacuum ovens are used for drying. Cleaning of non-continuous production equipment constitutes a major source of wastewater. Most PMN chemicals will fall into this subcategory.

Source: USEPA, 1974a

TABLE C-3. CATEGORIZATION OF WASTEWATER GENERATED BY 23 UNIT PROCESSES[1]

Subcategory A	Subcategory B	Subcategory C	Subcategory D
Acylation	Amination	Alcoholysis	Alkylation
Alkylation	Hydration	Ammonolysis	Amination
Aromatization	Dehydration	Dehydration	Condensation
Friedel-Crafts reactions	Hydrogenation	Esterification	Nitration
Halogenation	Dehydrogenation	Hydroformulation	
Hydrodealkylation	Oxidation	Hydration	
Isomerization	Pyrolysis	Neutralization	
Hydrohalogenation	Reforming (Steam) - Water Gas Reaction	Nitration	
	Ammoxidation	Oxidation	
	Condensation	Ammoxidation	
	Oxyhalogenation	Condensation	
	Halogenation	Amination by Ammonolysis	
	Catalytic Cracking	Sulfonation	
	Esterification	Carbonylation	
	Hydrohalogenation	Phosgenation	
	Dehydrohalogenation	Dehydrohalogenation	

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[1] Can fall into more than one subcategory because of different unit operations and different chemical conversions.

Source: Adopted from USEPA 1974a.

TABLE C-4. MAJOR RAW WASTE LOADS (RWL) OF POLLUTANTS BASED ON PROCESS WASTEWATER

Category	Flow RWL	BOD_5 RWL	COD RWL	TOC RWL
	gals/1,000 lbs	lbs/1,000 lbs	lbs/1,000 lbs	lbs/1,000 lbs
A	0.25 - 2,000	0.1 - 0.13	0.3 - 3.7	0.034 - 0.9
Conc. Range (mg/L)		(400 - 1,000)	(200 - 10,000)	(50 - 2,000)
B	50 - 3,000	0.09 - 7.0	0.47 - 21.5	0.2 - 40
Conc. Range (mg/L)		(50 - 500)	(200 - 5,000)	(100 - 2,000)
C	30 - 3,000	1.3 - 125	1.9 - 385	1.5 - 150
Conc. Range (mg/L)		(3,000 - 10,000)	(10,000 - 50,000)	(3,000 - 15,000)
D	10,000 - 100,000	52 - 220	180 - 4,800	60 - 1,600
Conc. Range (mg/L)		(100 - 3,000)	(1,000 - 10,000)	(200 - 2,000)

Source: USEPA 1974a.

TABLE C-5. TREATED WASTEWATER EFFLUENTS FOR POLYMERIZATION PROCESSES[1]

Subcategory I	Subcategory II	Subcategory III	Subcategory IV
Polyvinyl chloride	cellophane	polyester resin	acrylic resins
suspension		batch	
emulsion	rayon	continuous	
bulk			
	ABS/SAN	Nylon 66	
Polyvinyl acetate			
		Nylon 6	
Polystyrene			
suspension		cellulose acetate	
bulk			
Polypropylene			
Polyethylene			
low density			
high density			

Subcategory I - a low raw waste load: a raw waste load less than 10 units/1000 units of product.
- attainable low BOD$_5$ concentrations: less than 20 mg/liter.

Subcategory II - a high raw waste load: a raw waste load greater than 10 kg/kkg of product.
- attainable low BOD$_5$ concentrations.

Subcategory III - a high raw waste load.
- attainable medium BOD$_5$ concentrations: in the 30-75 mg/liter range.

Subcategory IV - a high raw waste load.
- attainable high BOD$_5$ concentrations: greater than 75 mg/liter.

[1] Source: USEPA, 1974b

TABLE C-6 ENVIRONMENTAL RELEASES FROM HEATING & COOLING EQUIPMENT

Equipment	Gaseous Emissions	Liquid Releases	Solid Wastes
Condensers	Fugitive emissions due to leaks[1] Some have vents to purge noncondensable by-product gases and/or to be used as pressure vents.[1]	Contaminated cooling liquid due to leaks, which is usually water that is sent to the cooling tower.[1]	None[1]
Partial condensers	Fugitive emissions due to leaks.[1] May have pressure-relief vents to purge noncondensable gases, not usually.[1] If uncondensed gases are unwanted, they are either vented from condenser or separated in vapor-liquid separator and vented atmosphere.[1]	Contaminated cooling water due to leaks, sent to cooling tower.[1] If condensed liquid is undesired after being separated in vapor-liquid separator, it will be a contaminated stream.[1]	None[1]
Quench tower	Fugitive emissions at fittings, valves, pumps, etc. Gases released from degassing quench liquid will be either vented, flared or recycled.[1]	Quench liquid comes in direct contact with products for a short contact time. This stream can be very contaminated depending on the contact time and the solubility of the gases in the quench liquid. If highly contaminated it will be treated in a degasser.	Degassed quench liquid may go to a settling tank, the bottoms of the settling tank will be landfilled[1].
Cooling towers	Entrained or dissolved hydrocarbons in the process water being cooled are discharged to the atmosphere.[1,2]	Waste waters from blowdown purge stream are contaminated with high-boiling liquids, oils and dissolved solids.[2]	Dissolved solids from blowdown stream.[2]
Heat Exchangers	None.[1]	Contaminated cooling or heating liquid, (mostly water) which is sent to cooling tower.	None.[1]
Preheaters	Combustion products may contain a small concentration of hydrocarbons (<1%), and oxides of nitrogen (NO_x) and sulfur compounds, depending on the feed (coal, oil or natural gas).[1,2]	None[1]	Sludge from bottom of bottom of preheater.[1]

TABLE C-6 CONTINUED

Equipment	Gaseous Emissions	Liquid Releases	Solid Wastes
Furnaces	Same gaseous emissions as preheaters.[1,2] Also hydrocarbon and coke particulates are emitted to the atmosphere when decoking furnaces.[1]	Wastewater from scrubbing decoking gases, if scrubbers are used.[1]	Landfill residual coke when decoking furnaces.[1]
Boilers	Same gaseous emissions as preheaters.[1,2]	Dissolved solids released in blowdown wastewater (0 - 4% of steam rate for steam evaporators).[3] Scale and sludge removed while cleaning using an acid cleaning solution, which must be further treated.[3]	Bottom ash consisting of slag, clinker and ash for coal-fired boilers and also fly ash.[3] Less than 0.1% ash for oil or gas-fired boilers.[3]
Driers	Incomplete combustion products of the fuel fired-oil or natural gas.[2] Off-gas vent used to purge violatizing products.[1] VOC emissions: 0.1 - 5.0 kg/kkg of product.[1]	Condensed liquid wastes after they have been evaporated out of the product.[1]	Leftover sludge from material being dried.[1]
Evaporators	Fugitive emissions due to leaks in the evaporators.[1] Off-gas vent used to purge undesired gases. NaOH recovery evaporators release 60 kg/kkg of VOC to air.[1]	Waste water releases during blowdown contains dissolved solids from feed.[3] Condensed liquid wastes after they have been evaporated from product.[1] VOC release 1.0 - 10.0 kg/kkg product.[1]	Dissolved solids from blowdown.[3] Sludge from thin film evaporators to water contain 1.0 - 200 kg VOC+ NaCl/kkg product.[1]

[1] Source: Adopted from Environmental Release Data Base, Appendix A.
Available emission factors came from less than 3 data points.
If no emission factors were available then the release is either not very serious or it has not been researched yet.

[2] Source: Bucon and Macko, 1978.

[3] Source: Aynsley and Jackson, 1971.

TABLE C-7 ENVIRONMENTAL RELEASES FROM ABSORPTION, DISTILLATION AND STRIPPER COLUMNS IN THE SOCMI

Unit Operation	Gaseous Emissions	Range of Release Data kg/kkg Product	# of SOCMI Chemicals[2]	Liquid Releases	Range of Release Data kg/kkg Product	# of SOCMI Chemicals[2]	Solid Wastes	Range of Release Data kg/kkg	# of SOCMI Chemicals[2]
Absorption including gas scrubbers	Large gaseous emission to purge the inert carrier gases. Generally halogenation type reactions and oxygen-related reactions use absorbers. The amount released depends on the stoichiometry and the excess reactants used. Columns may have packing which is regenerated.	Air for oxygen supply-N_2 emissions: 500 - 29,000 Inorganic inert-carrier gases: (CO_2, NO_x, H_2, HCl, Cl_2) 10 - 800 VOC inert-carrier gases: 10 - 200 VOC product: 0.1 - 10 kg/kkg Using ethanolamine sorbents which absorb H_2. When regenerated, SO_2: 1.2.	3 15 12 12 1	Contaminated absorbing liquid, generally from halogenation type processes, which absorb chlorides into absorbing liquid as a solution or a salt. Most plants use the control option that sends the wastewater to be degassed (recover HCl), neutralized and ponded. Look at stoichiometry and conversion to see how much Cl or HCl is produced or unreacted, these approximate amounts will exit in waste water or as a salt. Also look at the solubility of potential VOC in absorbing liquid.	VOC (including chlorinated VOCs) 0.1-5 Range varies depending on the stoichiometry.	4	none		
Distillation	Large gas emission from vents on columns in the condensing section. Dissolved or entrained gases are removed by these vents. Amount depends on the amount of by-product gases and lower boiling liquids which will still be in the product when it reaches the distillation section. Fugitive emissions will also occur from leaks in distillation.	VOC: 0-25 VOC: 0.5	43 1	If using extractive distillation, will have a contaminated extracting solvent after successive distillations.	N/A		Bottoms product containing higher boiling impurities from last column (usually) in process flow, may be a solid or a liquid waste. May be treated (if liquid) or landfilled or incinerated (if solid).	VOC: 1 - 100	40

TABLE C-7 CONTINUED

Unit Operation	Gaseous Emissions	Range of Release Data kg/kkg Product	# of SOCMI Chemicals[2]	Liquid Releases	Range of Release Data kg/kkg Product	# of SOCMI Chemicals[2]	Solid Wastes	Range of Release Data kg/kkg	# of SOCMI Chemicals[2]
Stripping including degassers	Continuous atmospheric emissions may result if spent stripping gases are vented or flared.	VOC: 0.001 - 150	14	Spent stripping gas may be condensed.	VOC: trace - 3.0 Inorganics: 10 - 200	1 4	Solid wastes extracted from stripper at blowdown	N/A	
	Fugitive emissions will occur from valves, fittings, etc.	N/A		Sludge may be released as wastewater from the column bottoms at blowdown.	N/A				

1. Source: Adopted from Environmental Release Data Base in Appendix A.

2. On which this kind of data are reported.

3. The contaminated stream will be gaseous or liquid depending on if the product is a liquid or a vapor, respectively. However, both streams can be contaminated for instance, when processing reactor off-gas to remove chlorides. The off-gas will be emitted to the air and the chlorides will be released to water.

TABLE G-8 RELEASE FROM SOME UNIT OPERATIONS IN THE SOCMI

Equipment	Gaseous Emissions	Range of Release Data kg/kkg Product	# of SOCMI Chemicals^2	Liquid Releases	Range of Release Data kg/kkg Product	# of SOCMI Chemicals^2	Solid Wastes	Range of Release Data kg/kkg	# of SOCMI Chemicals^2
Centrifuges	None			If desired product is a solid then will have a contaminated liquid waste stream.	VOC: 20	1	If desired product is a liquid then will have a contaminated solid waste.	NaCl: 431	1
Crystallizers	Particulate and hydrocarbon emissions from flaking.	VOC: 0.46	1	Wastewater can be created.	N/A		None		
Decanters	None			Liquid wastes containing oils or other undesired liquids, must be disposed of.	N/A		Solid waste will result if undesired liquid is a heavy sludge.	N/A	
Dehydrators drying columns may be using desiccants	Vent to atmosphere containing evaporated product and solvent vapors. Gaseous emissions containing hydrocarbons will result during regeneration of desiccants.	VOC: 0.052 - 2.5	5	Vapors and hydrocarbons in spent regenerating gas may be condensed and will form a contaminated wastewater. Bottoms of dehydrator column may be purged at blowdown.	VOC: 0.12 Ethanol: 4.8 (Alcohol dehydrator)	1 1	Disposal of desiccants after useful life is completed.	N/A	
Filters	None			Filter effluent wastewater may contain filter solids.	N/A		Filter residue to landfill.	Tars and carbon solids: 0.05-0.8 Filtercake $NaSO_3$:101.5	6 1
Filter Presses	VOC's can be emitted.			If desired product is solid, then a liquid wastestream will result.	N/A		If desired product is liquid, then solids will be disposed of.	N/A	
Flash Towers	Vent on column can have releases similar to distillation column vents, if the gas is unwanted. Fugitive emissions will occur from fittings, valves, etc.	See Table G-7 N/A		Liquid release if the liquid stream is unwanted.	N/A		Heavy residue in bottom of chamber will be removed at at blowdown.	N/A	
Neutralizers	Neutralizers may have vents.	VOC: 0.0107	1	Wastewater generated when neutralizing acidic or basic streams.	VOC (and chlorinated VOCs): trace - 10.0 Inorganic salts: 1.0 - 600	5 5	Precipitate formed may be dissolved in a liquid or a solid waste.	N/A	
Settling tanks and basins	None			Settling basin overflow released to water.	VOC: 7 - 50 Inorganic: 12.5 - 723	4	Heavy ends, tarry matter and slag in bottom of settling tank.	VOC:0.393 Inorganic: 100	2

TABLE C-8 CONTINUED

Equipment	Gaseous Emissions	Range of Release Data kg/kkg Product	# of SOCMI Chemicals^2	Liquid Releases	Range of Release Data kg/kkg Product	# of SOCMI Chemicals^2	Solid Wastes	Range of Release Data kg/kkg	# of SOCMI Chemicals^2
Steam Jet Ejectors	Gases pulled out when pulling a vacuum will contaminate steam. Steam is vented, not reused.	N/A		If steam is condensed then will have a contaminated water wastestream.	N/A		None.		
Vapor-Liquid Separators	If the desired product is liquid then the undesired gases may be vented to the atmopshere.	N/A		If the desired product is gaseous then the undesired liquid may form a liquid waste stream.	N/A		None.		
Water Washes	None.			Water will become contaminated with organics and inorganics. This water will be sent to a stripper to strip out the organics, then neutralized and ponded.	N/A		None.		

1. Source: adopted from Environmental Release Data Base in Appendix A.

2. On which this kind of data are reported.

TABLE C-9. POSSIBLE REACTOR RELEASES[1]

Type of Release	Source	Range of Release Data kg/kkg product	No. of SOCMI Chemicals[2]
Some reactors have off-gas vents	Excess reactants gases or by-product gases	VOC (including chlorinated VOC): 0.0005-50.0 Inorganics: 0.005-325	36
Liquid solvents left in reactor	Unwanted liquids separated in reactor by gravity	Catalysts, solvents (SO_2, HCl, NaCl) 28.6-125	4
Solid residues in reactor bottoms	Tarry matter and catalyst; Inorganics are released to water or land	VOC: 0.033-60 Inorganics: 28.6-400	8

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[1] Source: Adopted from the Environmental Release Data Base in Appendix A.

[2] On which this kind of data are reported.

TABLE C-10. NATIONWIDE UNIT OPERATIONS EMISSIONS CHARACTERISTICS IN THE SOCMI

Unit Operation	No. of Times Unit Operation Used in the SOCMI	Estimated Contributions to Total Unit Process Emissions (%)	Cumulative Contribution (%)
Absorption	475	58.1	58.1
Scrubbing/washing	543	27.9	86.0
Distillation	3651	10.4	96.4
Drying	251	3.3	99.7
Filtration	120	0.1	99.8
Extraction	110	0	99.8
Settling	24	0	99.8
Crystallization	144	0	99.8*
Separation	384		
Quenching	146		
Evaporation	127		
Ion exchange	120		
Dilution	71		
Mixing/blending	56		

*Less than 100 because of rounding errors.

Source: White 1980.

TABLE C-11. SOCMI UNIT OPERATIONS WASTE WATER EFFLUENTS

Water Enters Process Through Unit Operations

1. Direct-contact quenching
2. Absorption of gaseous chemicals in water
3. Scrubbing of less volatile chemicals from a gaseous product stream
4. Stripping of more volatile chemicals from a product stream (water enters as steam)
5. Vacuum distillation columns and the associated condensate from steam jet ejectors
6. Washing of chemicals from solid products
7. Washing or purging process lines and equipment in batch sequence operations

Water Leaves the Process Through Unit Operations

1. Liquid-liquid separation equipment, such as decant drums.
2. Vapor-liquid separation equipment, such as distillation columns or flash chambers.
3. Solid-liquid separation equipment, such as crystallizers, filters, centrifuges.

Non-Contact Water

1. Used as heating or cooling medium in heat exchanges, condensers, reboilers, evaporators, and jacketed reactors.

Source: USEPA, 1974a

TABLE C-12. SOCMI UNIT OPERATIONS WHICH GENERATE SOLID WASTES

1. Bottoms product of distillation columns
2. Filter residue from filters
3. Centrifuge solids from centrifuge
4. Bottoms of settling tanks
5. Blowdown of equipment

Source: Adopted from the Environmental Release Data Base, in Appendix A

TABLE C-13. EQUATIONS USED FOR CALCULATING AIR EMISSIONS FOR INERT-CARRIER GAS METHOD (USING CHLORINATION REACTIONS AS AN EXAMPLE)

$$a\,R + b\,Cl_2 \longrightarrow c\,RCl + d\,HCl$$

$$G = C + H + R + P \qquad (1)$$

where

G = the molar ratio of total reaction-related carrier-gas flow from the reactor after processes by any separation-recovery equipment to the production rate,

C = the molar ratio of chlorine-related carrier-gas flow to the production rate,

H = the molar ratio of hydrogen chloride-related carrier-gas flow to the production rate,

R = the molar ratio of gaseous organic reactants carrier-gas flow to the production rate,

P = the molar ratio of gaseous organic products carrier-gas flow to the production rate,

In turn the molar ratio of chlorine related carrier gases, C, is expressed as

$$C = \left[MCR \times (F_C - 1) \times (1 - S_C)\right] + \left[MCR \times (1 - P_C) \times F_C \times (1 - S_{IN})\right] \qquad (2)$$
$$(F_C - 1 = 0 \text{ if } F_C \leq 1),$$

where

MCR = the molar ratio of chlorine to product,

P_C = the molar purity of the chlorine,

F_C = the molar ratio of total chlorine feed to the stoichiometric requirement, this includes excess and unreacted chlorine,

S_C = the separation efficiency of chlorine in the separation-recovery equipment following the reaction,

S_{IN} = the separation efficiency of the gaseous impurities in the chlorine in the separation-recovery equipment following the reaction.

The molar ratio of hydrogen chloride-related carrier gases, H, is

$$H = MCHR \times (1 - S_H), \qquad (3)$$

where MCHR = the molar ratio of hydrogen chloride to product, and S_H is the separation efficiency of hydrogen chloride in the separation-recovery requipment following the reaction.

TABLE C-13. EQUATIONS USED FOR CALCULATING AIR EMISSIONS FOR INERT-CARRIER GAS METHOD (USING CHLORINATION REACTIONS AS AN EXAMPLE)

$$a\,R + b\,Cl_2 \longrightarrow c\,RCl + d\,HCl$$

(continued)

The molar ratio of gaseous organic reactant carrier gases, R, is

$$R = MGRR \times F_{GR} \times (1 - Y_{GR}) \times (1 - S_{GR}), \qquad (4)$$

where

MGRR = the molar ratio of gaseous organic reactant to product,

F_{GR} = the molar ratio of total gaseous organic reactant to the stoichiometric requirement,

Y_{GR} = the molar overall reaction yield on the gaseous organic reactants,

S_{GR} = the separation efficiency of the gaseous organic reactants in the separation-recovery equipment following the reaction.

The molar ratio of gaseous organic product carrier gases, P, is given as

$$P = MGPR \times (1 - S_{GP}), \qquad (5)$$

where MGPR is the molar ratio of gaseous organic product to product manufactured, and S_{GP} is the separation efficiency of the gaseous organic products in the separation-recovery equipment following the reaction.

Conversion of G (molar ratio) to G(scfm/annual production)

$$G\left(\frac{\text{scfm}}{\text{annual production}}\right) = G\left(\frac{\text{moles of gas}}{\text{moles of product}}\right) \times \frac{359\ \text{scf}}{1\ \text{lbmole of gas}} \times \frac{1\ \text{lbmole of product}}{\text{MW product (lbs)}} \times$$

$$\frac{\text{production-volume (kkg)}}{\text{yr}} \times \frac{2.2046\ \text{lb}}{\text{kg}} \times \frac{1000\ \text{kg}}{\text{kkg}} \times \frac{1\ \text{yr}}{\text{minutes in operation}} \qquad (6)$$

This yields the total gas flow being released from the entire process for the proposed annual production.

Calculation of carrier-gas VOC in reactants and products

1.) Pick the most volatile reactant and product

2.) Use the variable R for reactant VOC

3.) Convert R into $\frac{\text{scfm}}{\text{annual production}}$ as shown above for G. (Note: MW is the MW of the product)

4.) $$R\left(\frac{\text{kkg of VOC}}{\text{yr}}\right) = R\left(\frac{\text{scfm}}{\text{annual production}}\right) \times \frac{\text{minutes in operation}}{\text{yr}} \times \frac{1\ \text{lbmole of gas}}{359\ \text{scf}} \times \frac{MW_{VOC}}{1\ \text{lbmole}} \times \frac{1\ \text{kg}}{2.2046\ \text{lbs}} \times \frac{\text{kkg}}{1000\ \text{kg}}$$

TABLE C-13. EQUATIONS USED FOR CALCULATING AIR EMISSIONS FOR INERT-CARRIER GAS METHOD (USING CHLORINATION REACTIONS AS AN EXAMPLE)

$$a\,R + b\,Cl_2 \longrightarrow c\,RCl + d\,HCl$$

(continued)

5.) Use the variable P for product VOC and pick the most volatile product.
6.) Perform steps 3 and 4 on the variable P.

This yields the amount of VOC contained in the reactant and product gases that escape to the atmosphere.

Calculation of VOC Released From Organic Liquids and Solids

1.) Pick the most volatile organic liquid or solid.

2.) The equation for the estimation VOC from organic liquids or solids is shown below:

$$Y_{VOC} = A \sum_{i=1}^{n} x_i \frac{P_i^*}{\pi} \qquad (7)$$

where

Y_{VOC} = the mole fraction of organic vapors (VOC) arising from gas contacting liquid or solid organic compounds,

A = the fractional approach to saturation ($A = 1$ for a saturated vapor), Saturation is assumed for worst case.

n = the number of organic compounds present in the liquid or solid,

x_i = the mole fraction of organic component i in the liquid,

P_i^* = the vapor pressure of the ith organic compound at the temperature of the emission,

π = the total pressure (normally atmospheric) at the emission point.

Since we are interested in the range for VOC emissions, Y_{VOC} is calculated for the single most volatile liquid present in the chlorination reaction as if it were the only organic present. Saturation is also assumed. Therefore equation IV-7 is simplified to

3.) $$Y_{VOC} = \frac{P_i^*(\text{mm Hg})}{760} \qquad (8)$$

4.) $$VOC\left(\frac{\text{scfm}}{\text{annual production}}\right) = G\left(\frac{\text{scfm}}{\text{annual production}}\right) \times \frac{Y_{VOC}}{1-Y_{VOC}}$$

Use the fraction $Y_{VOC}/(1-Y_{VOC})$ because G is not the total flow.

The total release to air = G + VOC from the entire process for the proposed annual production, this includes the total inert carrier-gas flow and also the volatilizing liquids.

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[1] Source: Blackburn, J.W. March 1981. Emissions Projections for Carrier-Gas-Producing Reactions, prepared for USEPA/OAQPS, Research Triangle Park, North Carolina, under the aegis of EPA Contract No. 68-02-2577.

TABLE C-14. EQUATIONS USED FOR CALCULATING AIR EMISSIONS FOR REACTION USING AIR AS ITS SOURCE OF OXYGEN[1]

The total flow of gases exiting the process through condenser or absorber vents after reaction is described by the variable, S_2.

$$S_2 = A + R + O + W \qquad (1)$$

where

A = the air-carrier gases not removed by the separation equipment,

R = the reaction-carrier gases not removed by the separation equipment,

O = the oxidation reaction-carrier gases not removed by the separation equipment,

W = the water to saturate the gases at 100°F.

The total quantity of air-source gases in lbmoles/hr, A, may be expressed by the following equation:

$$A = \frac{4.76 \text{ lbmoles of air}}{\text{lbmole of } O_2} \times \frac{CAP}{MW_p} \times MOR \times F \qquad (2)$$

where

CAP = plant capacity (lb/hr),

MW_p = product molecular weight (lb/lbmole of product),

MOR = stoichiometric molar oxygen ratio (lbmoles of O_2/lbmole of product),

F = ratio of actual air to reactor/theoretical stoichiometric air requirement.

However, since the inert nitrogen in air will be emitted in much larger quantitites than any of the other gases, it is safe to say within the accuracy of design that the total gas flow is equal to the air-carrier gas flow. ($S_2 = A$)

$$\text{Total reactor off-gas in lb-moles/hr} = \frac{4.76 \text{ lbmoles of air}}{\text{lbmole of } O_2} \times \frac{CAP}{MW_p} \times MOR \times F \qquad (3)$$

The total gas released from the process will be S_2 + VOC. The total VOC can be evaluated from actual plant data available. It is known that 11 plants show all off-gas emissions to contain less than 5% VOC (White, 1980). Therefore, as a worst case we will say that the total gas released from the process will be $S_2 + 0.05\, S_2$.

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[1] Source: Blackburn, J.W. December 1980. Air Oxidation Emission Projections, prepared for USEPA/OAQPS, Research Triangle Park, North Carolina, under the aegis of EPA Contract No. 68-01-2577.

REFERENCES

Aynsley, Eric, and Meryl R. Jackson. 1971. Industrial Waste Studies: Steam Generating Plants. Prepared for USEPA - Water Quality Office, Washington, D.C.

Bucon, H. W., and J. Macko. 1978. Volatile Organic Compound (VOC) Species Data Manual. Prepared for USEPA, Research Triangle Park, North Carolina.

Blackburn, J.W. December 1980. Air Oxidation Emission Projections, prepared for USEPA/OAQPS, Research Triangle Park, North Carolina, under the aegis of EPA Contract No. 68-01-2577.

U.S. EPA. 1974a. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemical Manufacturing. Point Source Category. Washington, D.C.

U.S. EPA. 1974b. U.S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Synthetic Resin Segment of the Plastics and Synthetic Materials Manufacturing Point Source Category. Washington, D.C.: U.S. EPA.

White, R. E. IT Enviroscience. 1980. Organic Chemical Manufacturing. Volumes 6-10. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina: EPA-450/3-80-028.